Supporting information for:

Toward an Understanding of 1,5 Asymmetric Induction During Nucleophilic Addition to Arenechromium Tricarbonyl Complexes: Conformational Preference of the Chromium Tricarbonyl Tripod for Transmission of Chirality.

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Contents:

General procedures: All reactions involving chromium tricarbonyl complexes were performed using oven-dried (125 ºC) glassware under anhydrous, oxygen free argon atmosphere. All reactions were performed in freshly distilled (under nitrogen) solvents and monitored by TLC on silica gel. The TLC plates were visualized with UV light and/or with phosphomolybdic acid solution in ethanol (12.5 g in 100 mL of ethanol). Reactions performed at -60 ºC were maintained at that temperature using ethanol bath and Neslab Cryotrol. Flash chromatography was performed on silica gel with mesh 170-400 under nitrogen pressure. NMR spectra were recorded on a Varian Gemini 200 (200 MHz) or Varian Gemini 300 (300 MHz) or Varian Inova 600 (600 MHz) spectrometer. FTIR spectra were

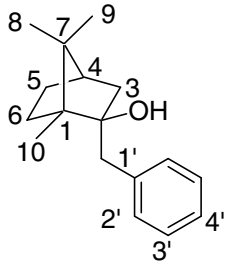
recorded as neat oils or KBr pellet on a Nicolet Impact 400 FTIR spectrometer. High resolution mass spectra (HRMS) of compounds were recorded in-house using a Kratos MS25A instrument by either EI (Electron Ionization) or FAB (Fast Atom Bombardment). Capillary GC was carried out using HP5890 Series II Gas Chromatograph. The melting points were measured on a Thomas Hoover apparatus and are uncorrected. The melting points of arene chromium tricarbonyl complexes are not reported because of the consistent decomposition of the complexes when heating in a capillary tube. The purity of new compounds was assessed from their ^{1}H and ^{13}C NMR spectra. The chemical shifts are assigned for these compounds as it is necessary for understanding the conformational studies.
NMR experiments - General. The NOE ^{1}H NMR experiments were carried out using Varian Inova 600 MHz spectrometer at room temperature (23-25 ºC) in THF-d_8 (Aldrich) or $CDCl_3$ (Norrell Inc.) or C_6D_6 (Norrell Inc.) as solvent. The solvents for ^{1}H and ^{13}C NMR were referenced respectively as follows, $CDCl_3$: 7.26 ppm & 77.0 ppm, C_6D_6: 7.17 ppm & 128.0 ppm, THF-d_8: 3.61 ppm & 67.4 ppm.

General Procedure for Preparation of C2 substituted chiral isoborneols (From a procedure reported by Dimitrov, V. *et al*)[1]: In an oven dried round bottom flask with stirrer, anhydrous cerium chloride, and D-(+) Camphor (99.5% from Acros) were mixed. Freshly distilled and cooled THF was added and the slurry was stirred at room temperature. After approximately 2 h the corresponding Grignard reagent was added dropwise via a syringe or through a canula under nitrogen atmosphere. Usually there is a slight color change from white to yellow or grey slurry. The progress of reaction was checked with tlc and GC. The workup involves very slow dropwise addition of saturated ammonium chloride solution until the grey/yellow slurry separates into a solid and a clear organic solution. The supernatant was removed and the solid precipitate washed thrice with diethyl ether. The washings were combined and dried ($MgSO_4$), filtered and the solvent was evaporated. The isoborneols were obtained as sweet smelling white solids or colorless oils. Solids were purified by recrystallization and oils were purified by flash column chromatography.

The known chiral C2 isoborneols (1*R*, 2*S*)-1,7,7-trimethyl-2-phenylbicyclo[2.2.1]heptan-2-ol (**2a**), (1*R*,2*S*)-1,2,7,7-tetramethylbicyclo[2.2.1] heptan-2-ol (**2b**) and (1*R*, 2*S*)-1,7,7-trimethyl-

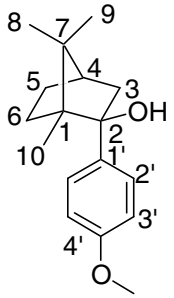
2-ethylbicyclo[2.2.1]heptan-2-ol (**2h**) were prepared using the aforementioned general procedure, using the corresponding Grignard reagents while, spiro[(*1R*, 2*S*)-1,7,7-trimethylbicyclo[2.2.1]heptane-3,2'-[1,3]dioxalan]-2-ol (**2c**) was prepared by a reported procedure.[2] NMR characterization and specific rotation values matched with those reported in the literature and are not included here.

(1*R*, 2*S*)-1,7,7-Trimethyl-2-benzylbicyclo[2.2.1]heptan-2-ol (2d) was prepared as a colorless oil from *D*-(+) camphor and benzylmagnesium chloride in THF.



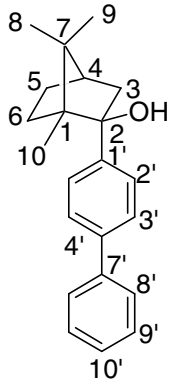
Yield: 79%; R_f: 0.45 (9:1 hexane/ethyl acetate); EI HRMS *m/z* 244.1825 (M^+), calcd for $C_{17}H_{24}O$ 244.1827; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.22 (5H), 2.81 (2H, J_{AB} = 13.2 Hz), 1.82 – 1.75 (3H), 1.68 – 1.62 (2H), 1.52 – 1.44 (1H, m), 1.41 (1H, s), 1.19 – 1.12 (1H, m), 1.08 (3H, s), 0.88 (3H, s), 0.82 (3H, s); ^{13}C NMR and APT (50 MHz, $CDCl_3$) δ 138.1 (C1'), 130.7 (C2' and C6'), 128.3 (C3' and C5'), 126.5 (C4'), 80.2 (C2), 52.7 (C1), 49.3 (C7), 46.2 (C3), 45.2 (C4), 44.7 (-$\underline{C}H_2$-Ph), 30.5 (C6), 27.2 (C5), 21.6 (C8 or C9), 21.1 (C8 or C9), 10.4 (C10). FTIR (KBr) ν_{max} 3585, 3033, 2954, 2875, 1499, 1460, 1124cm^{-1}.

(1*R*, 2*S*)-1,7,7-Trimethyl-2-[4-methoxyphenyl]bicyclo[2.2.1]heptan-2-ol (2e) was prepared as a white crystalline solid from *D*-(+) camphor and 4-methoxyphenylmagnesium bromide (prepared fresh from magnesium pellets and 4-bromoanisole) in THF.



Yield: 91%; $[\alpha]^{22}_D$ = -20.62 (*c* = 2.42 g/100 mL , $CHCl_3$); R_f: 0.22 (10:1 hexane/ether); FAB HRMS *m/z* 260.1726 (M^+), calcd for $C_{17}H_{24}O_2$; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.45 (2H, d, *J* = 8.8 Hz), 6.87 (2H, d, *J* = 8.8 Hz), 3.82 (3H, s, -O-C<u>H</u>$_3$), 2.29 (1H, d, *J* = 13.8 Hz), 2.18 (1H, dt, *J* = 14.2, 3.1 Hz), 1.90 (1H, t, *J* = 4.2 Hz), 1.84 (1H, s), 1.82 – 1.66 (1H, m), 1.28 (3H, s), 1.25 – 1.12 (2H), 0.92 (3H, s), 0.91 (3H, s), 0.87 – 0.79 (1H, m); ^{13}C NMR and APT (50 MHz, $CDCl_3$) δ 158.5 (C4'), 138.4 (C1'), 127.9 (C2' & C6'), 112.9 (C3' & C5'), 83.4 (C2), 55.3 (-O-<u>C</u>H_3), 53.6 (C1), 50.4 (C7), 45.68 (C4), 45.66 (C3), 31.4 (C6), 26.7 (C5), 21.8 (C8 or C9), 21.7 (C8 or C9), 9.9 (C10). FTIR (KBr) ν_{max} 3590, 2934 cm^{-1}.

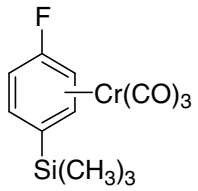
(1*R*, 2*S*)-1,7,7-Trimethyl-2-[4-biphenyl]bicyclo[2.2.1]heptan-2-ol (2f) was prepared as a white crystalline solid from *D*-(+) camphor and 4-biphenylmagnesium bromide (prepared fresh from magnesium pellets and 4-biphenylbromide) in THF.



Yield: 86%; mp = 120 – 121 °C; $[\alpha]^{25}_D$ = - 22.12 (*c* = 2.31 g/100 mL, $CHCl_3$); R_f: 0.31 (10:1 hexane/ether); FAB HRMS *m/z* 305.1939 (M^+-H), calcd for $C_{22}H_{16}O$ 305.1905; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.66 – 7.32 (9H, m), 2.38 (1H, d, *J* = 14.0 Hz), 2.24 (1H, ddd, *J* = 14.0, 4.1, 3.1 Hz), 1.95 (1H, dd = t, *J* = 4.2 Hz), 1.88 (1H, s), 1.85 – 1.69 (1H, m), 1.37 – 1.17 (2H), 1.03 – 0.87 (1H, m), 1.31 (3H, s), 0.97 (3H, s), 0.95 (3H, s); ^{13}C NMR and APT (50 MHz, $CDCl_3$) δ 145.3 (C1'), 140.8 (C4'), 139.6 (C7'), 128.8, 127.3, 127.1, 126.3 (preceding 4 signals aromatic C-H carbons), 83.6 (C2), 53.6 (C1), 50.5 (C7), 45.71 (C3), 45.70 (C4), 31.4 (C6), 26.7 (C5), 21.74 (C8 or C9), 21.72 (C8 or C9), 10.0 (C10). FTIR (KBr) ν_{max} 3489, 2951, 2880 cm^{-1}.

η^6-(4-fluoro(trimethylsilyl)benzene)chromium tricarbonyl (4) was prepared from the corresponding arene by the Pauson and Mahaffy procedure[3] of refluxing the arene with

chromium hexacarbonyl (Strem chemicals) in a mixture of di-*n*-butyl ether and THF. 4-Fluoro(trimethylsilyl)benzene was prepared from commercially available 4-fluorobromo benzene by the published procedure.[4] The yellow crystalline chromium complex **4** was purified by recrystallization from 1:1 hexane/dichloromethane mixture and washed with ice cold hexane.

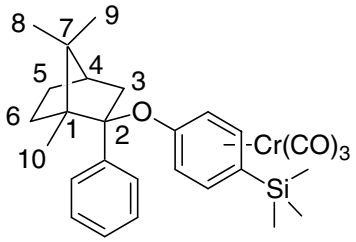


Yield: 71%; R_f: 0.48 (20:1 hexane/ether); FAB HRMS *m/z* 304.0025 (M^+), calcd for $C_{12}H_{13}O_4FSiCr$ 304.0023; ^1H NMR (200 MHz, $CDCl_3$) δ 5.52 (2H, dd, *J* = 3.6, 6.3 Hz, H *meta* to fluoro), 5.29 (2H, dd = t, *J* = 5.7 Hz, H *ortho* to fluoro), 0.28 (9H, s, -Si($C\underline{H}_3$)$_3$); ^{13}C NMR and APT (50 MHz, $CDCl_3$) δ 232.5 ($\underline{C}O$), 148.0 (d, J_{C-F} = 266.2 Hz), 98.5 (d, *J* = 6.6 Hz), 95.3 (arene($\underline{C}$)-Si(CH_3)$_3$, 79.0 (d, *J* = 18.3 Hz), -1.2 (-Si($\underline{C}H_3$)$_3$). FTIR (KBr) ν_{max} 3105, 1968, 1914, 1867 cm^{-1}.

General procedure for synthesizing alkoxy arenechromium complexes:

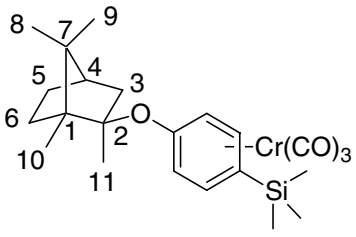
To a heterogeneous mixture of potassium hydride (20 % dispersion in mineral oil; 4.5 mmol, 1.5 equiv, washed thrice with freshly distilled diethyl ether to remove the mineral oil), in anhydrous diethyl ether (12 mL) at 0 ºC under argon, was added a solution of the chiral isoborneol (3.3 mmol, 1.1 equiv), in diethyl ether (6 mL), dropwise so that the hydrogen gas effervescence is not too vigorous. One hour after the hydrogen gas evolution had stopped, a solution of **4** (3 mmol, 1 equiv) in ether (9 mL) was added dropwise. The S_NAr reaction was complete after 4 h as indicated by TLC. The dark brown mixture was carefully quenched by slow addition of 5% aqueous hydrochloric acid or an aqueous solution of ammonium chloride. The aqueous phase was then extracted with ether (3 x 25 mL) and the combined ether extracts were washed with water, dried ($MgSO_4$), then filtered and concentrated *in vacuo* to give a yellow oil or solid. The crude product was purified either by recrystallization from 1:1 mixture of hexane/dichloromethane, which usually gave yellow crystals which were washed with cold hexane or purified by flash chromatography on silica gel (hexanes-ethyl acetate or hexanes-ether as eluent system).

η^6-{4-[[(1*R*,2*S*)-1,7,7-Trimethyl-2-phenyl)bicyclo[2.2.1]hept-2-yl]oxy]trimethylsilylbenzene}chromium tricarbonyl (3a) was prepared from phenyl isoborneol **2a** and **4**. Recrystallization with 1:1 hexane/methylene chloride gave rhombic yellow crystals.



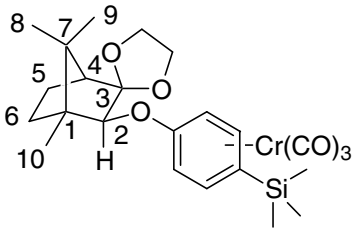
Yield: 86%; R_f: 0.31 (20:1 hexane/ether); FAB HRMS *m/z* 514.1629 (M^+), calcd for $C_{28}H_{34}O_4SiCr$ 514.1631; ^{1}H NMR (600 MHz, THF-d_8) δ 7.58 (1H, d, *J* = 7.8 Hz), 7.50 (1H, d, *J* = 7.8 Hz), 7.41 (1H, t, *J* = 7.5 Hz), 7.36 – 7.30 (2H, m), 5.55 (1H, d, *J* = 7.0 Hz), 5.48 (1H, d, *J* = 7.0 Hz), 4.95 (1H, dd, *J* = 6.9, 1.5 Hz), 4.87 (1H, dd, *J* = 6.9, 1.5 Hz), 2.53 (1H, d, *J* = 14.4 Hz), 2.45 (1H, d, *J* = 14.4 Hz), 1.96 (1H, t, *J* = 4.2 Hz), 1.80 – 1.77 (1H, m), 1.40 – 1.35 (1H, m), 1.23 (3H, s), 1.03 (3H, s), 0.99 (3H, s), 1.25 – 1.20 (1H, m), 0.85 – 0.80 (1H, m), 0.21 (9H, s, -Si(C$\underline{H}_3)_3$); ^{13}C NMR (150 MHz, THF-d_8) δ 235.0 (C$\underline{O}$), 143.0 (C$\underline{(}$arene complex)-O-), 140.8 (C$\underline{(}$phenyl)-C2), 129.0, 128.9, 128.8, 128.6, 126.6 (preceding five signals correspond to five C$\underline{-}$H carbons of the phenyl group), 102.3 (C$\underline{-}$*ortho* to TMS), 101.5 (C$\underline{-}$*ortho* to TMS), 93.9 (C$\underline{-}$TMS or C2), 93.7 (C$\underline{-}$TMS or C2), 84.5 (C$\underline{-}$*meta* to TMS), 83.7 (C$\underline{-}$*meta* to TMS), 55.8 (C1), 51.1 (C7), 46.4 (C4), 39.9 (C3), 31.1 (C6), 26.4 (C5), 22.0 (C8 or C9), 21.9 (C8 or C9), 10.2 (C10), -1.3 (-Si(C$\underline{H}_3)_3$). FTIR (KBr) ν_{max} 2934, 1966, 1885 cm^{-1}.

η^6-{4-[[(1*R*,2*R*)-1,2,7,7-Tetramethylbicyclo[2.2.1]hept-2-yl]oxy]trimethylsilylbenzene}chromium tricarbonyl (3b) was prepared from methyl isoborneol **2b** and **4** as a greenish yellow solid.



Yield: 97%; R_f: 0.75 (4:1 hexane/ethyl acetate); FAB HRMS *m/z* 452.1467 (M^+), calcd for $C_{23}H_{32}O_4SiCr$ 452.1475; ^{1}H NMR (600 MHz, THF-d_8) δ 5.73 (2H, m), 5.27 (1H, dd, *J* = 6.9, 2.1 Hz), 5.13 (1H, dd, *J* = 6.9, 2.1 Hz), 2.51 (1H, dt, *J* = 13.2, 3.6 Hz), 1.60 (3H, s), 1.55 (1H, t, *J* = 6.6 Hz), 1.51 – 1.46 (1H, m), 1.32 (3H, s), 1.16 – 1.11 (1H, m), 0.99 (3H, s), 0.97 – 0.88 (3H), 0.94 (3H, s), 0.28 (9H, s); ^{13}C NMR & APT (50 MHz, THF-d_8) δ 235.1 (C=O), 141.8 (C(arene complex)-O-), 102.2 (C-*ortho* to TMS), 101.4 (C-*ortho* to TMS), 93.2 (C-TMS or C2), 91.0 (C-TMS or C2), 83.0 (corresponds to two C-*meta* to TMS), 55.0 (C1), 49.5 (C7), 46.8 (C4), 44.4 (C3), 31.2 (C6), 26.9 (C5), 21.3 (C8 or C9 or C11), 21.2 (C8 or C9 or C11), 20.9 (C8 or C9 or C11), 10.4 (C10), -1.2 (-Si(CH_3)$_3$); FTIR (KBr) ν_{max} 2947, 2888, 1960, 1865 cm^{-1}.

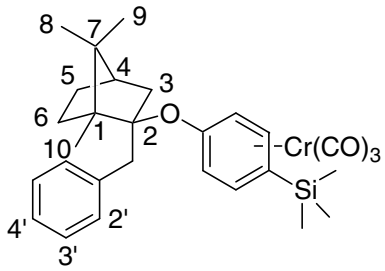
η^6-{4-[[[Spiro[(1*R*,2*S*)-1,7,7-trimethylbicyclo[2.2.1]heptane-3,2'-[1,3]dioxalan]-2-yl]oxy]trimethylsilylbenzene}chromium tricarbonyl (3c) was prepared from Spiro[(*1R*, 2*S*)-1,7,7-trimethylbicyclo[2.2.1]heptane-3,2'-[1,3]dioxalan]-2-ol[5] **2c** as a yellow solid.



Yield: 79%; R_f: 0.64 (4:1 hexane/ethylacetate); FAB HRMS *m/z* 496.1370 (M^+), calcd for $C_{24}H_{32}O_6SiCr$ 496.1373; ^{1}H NMR (600 MHz, C_6D_6) δ 5.16 (1H, dd, *J* = 6.9, 0.9 Hz), 5.12 (1H, dd, *J* = 6.9, 2.1 Hz), 5.02 (1H, dd, *J* = 6.9, 0.9 Hz), 4.85 (1H, dd, *J* = 6.9, 2.1 Hz), 4.01 (1H, s), 3.47 – 3.44 (1H, m), 3.29 – 3.26 (1H, m), 3.25 – 3.17 (2H), 1.73 -1.69 (1H, m), 1.49 – 1.44 (1H, m), 1.41 – 1.35 (2H), 1.35 (3H, s), 1.31 – 1.26 (1H, m), 1.15 (3H, s), 0.75 (3H, s), 0.12 (9H, s, -Si(CH_3)$_3$); ^{13}C NMR and APT (50 MHz, C_6D_6) δ 234.4 (C=O), 144.8 (C(arene complex)-O-), 115.3 (C3),100.7 (C-*ortho* to TMS), 99.3 (C-*ortho* to TMS), 92.3 (C(arene complex)-TMS), 89.7 (C2), 81.1 (C-*meta* to TMS), 78.3 (C-*meta* to TMS), 64.2 (-O-(CH_2)$_2$-O-), 63.7 (-O-(CH_2)$_2$-O-), 51.9 (C4), 49.8 (C1 or C7), 48.1 (C1 or C7), 33.9 (C6), 21.0 (C8 or C9), 20.9 (C8 or C9), 20.3 (C5), 11.2 (C10), -1.4 (-Si(CH_3)$_3$); ^{1}H NMR (600 MHz, THF-d_8) δ 5.77 (1H, d, *J* = 6.6 Hz), 5.73 (1H, d, *J* = 6.6 Hz), 5.32 (1H, dd, *J* = 7.2, 1.8 Hz), 5.29 (1H, dd, *J* = 7.2, 1.8 Hz), 4.07 – 4.02 (1H, m), 3.92 (1H, s), 3.90 – 3.73 (3H), 1.68 – 1.64 (1H, m), 1.61 – 1.56 (1H, m), 1.42 – 1.29 (2H), 1.16 (3H, s), 1.01 (3H, s), 0.95 – 0.83

(1H, s), 0.89 (3H, s), 0.28 (9H, s, -Si(C$\underline{H}_3)_3$); ^{13}C NMR and APT (50 MHz, THF-d_8) δ 235.2 (C$\underline{O}$), 145.9 (C$\underline{}$(arene complex)-O-), 115.6 (C3),102.2 (C$\underline{}$-*ortho* to TMS), 101.2 (C$\underline{}$-*ortho* to TMS), 93.6 (C$\underline{}$(arene complex)-TMS), 90.7 (C2), 82.4 (C$\underline{}$-*meta* to TMS), 79.7 (C$\underline{}$-*meta* to TMS), 65.3 (-O-(C$\underline{H}_2)_2$-O-), 64.8 (-O-(C$\underline{H}_2)_2$-O-), 52.8 (C4), 50.4 (C1 or C7), 48.7 (C1 or C7), 34.5 (C6), 30.5 (C5), 21.4 (C8 or C9), 20.8 (C8 or C9), 11.5 (C10), -1.1 (-Si(C$\underline{H}_3)_3$). FTIR (KBr) ν_{max} 2954, 1966, 1885, 1874 cm^{-1}.

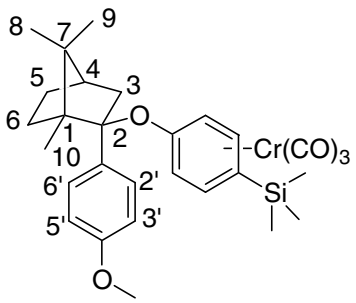
η^6-{4-[[(1*R*,2*S*)-1,7,7-Trimethyl-2-benzylbicyclo[2.2.1]hept-2-yl]oxy]trimethylsilylbenzene}chromium tricarbonyl (3d) was prepared from benzyl isoborneol **2d** and **4** as a yellow solid which on recrystallization from 1:1 hexane/methylene chloride yielded yellow rhombic crystals.



Yield: 73%; R_f: 0.45 (20:1 hexane/ether); FAB HRMS *m/z* 528.1786 (M^+), calcd for $C_{29}H_{36}O_4SiCr$ 528.1788; ^{1}H NMR (600 MHz, THF-d_8) δ 7.25 (2H, d, *J* = 7.2 Hz), 7.20 (2H, d, *J* = 7.2 Hz), 7.17 (1H, d, *J* = 7.2 Hz), 5.74 (1H, d, *J* = 7.2 Hz), 5.67 (1H, d, *J* = 7.2 Hz), 5.51 (1H, d, *J* = 7.2 Hz), 5.36 (1H, d, *J* = 6.6 Hz), 3.92 (1H, d, *J* = 16.2 Hz), 2.90 (1H, d, *J* = 15.6 Hz), 2.00 (1H, t, *J* = 9.9 Hz), 1.81 (1H, d, *J* = 13.2 Hz), 1.69 (1H, d, *J* = 13.2 Hz), 1.49 – 1.40 (1H, m), 1.24 – 1.19 (1H, m), 1.07 (3H, s), 0.87 (3H, s), 0.59 (3H, s), 0.31 (9H, s, -Si(C$\underline{H}_3)_3$); ^{13}C NMR & APT (50 MHz, THF-d_8) δ 235.0 (C$\underline{O}$), 142.9 (C$\underline{}$(arene complex)-O-), 139.0 (C$\underline{}$(aromatic)-CH_2-), 131.6 (C3'), 128.8 (C2'), 127.2 (C4'), 100.9 (C$\underline{}$-*ortho* to TMS), 100.1 (C$\underline{}$-*ortho* to TMS), 95.5 (C$\underline{}$-TMS or C2), 94.1 (C$\underline{}$-TMS or C2), 84.9 (C$\underline{}$-*meta* to TMS), 84.7 (C$\underline{}$-*meta* to TMS), 55.6 (C1), 50.8 (C7), 46.2 (C4), 43.9 (-C$\underline{H}_2$-Ph), 40.8 (C3), 31.1 (C6), 27.0 (C5), 22.0 (C8 or C9), 21.1 (C8 or C9), 11.8 (C10), -1.3 (-Si(C$\underline{H}_3)_3$). FTIR (KBr) ν_{max} 2967, 2921 (C-H stretch), 1966, 1885 (carbonyl) cm^{-1}.

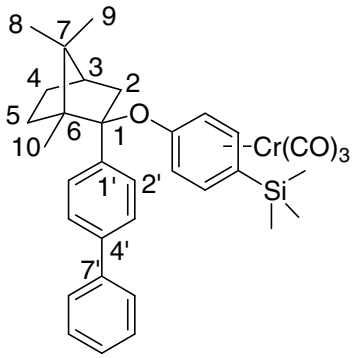
η^6-{4-[[(1*R*,2*S*)-1,7,7-Trimethyl-2-(4-methoxyphenyl)bicyclo[2.2.1]hept-2-yl]oxy]trimethylsilylbenzene}chromium tricarbonyl (3e) was prepared from anisyl

isoborneol **2e** as a yellow oil and purified by flash column chromatography (9:1 hexanes/ethyl acetate) to yield a yellow powder.



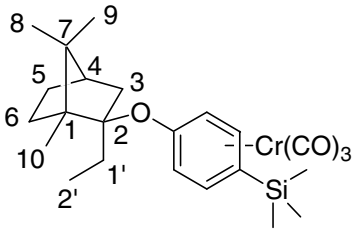
Yield: 87%; R_f: 0.29 (20:1 hexane/ether); FAB HRMS *m/z* 543.1663 (M^+-H), calcd for $C_{29}H_{36}O_5SiCr$ 544.1737; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (1H, dd, *J* = 8.1, 2.1 Hz), 7.30 (1H, dd, *J* = 8.1, 2.1 Hz), 6.90 (2H, dt, *J* = 11.4, 3.0 Hz), 5.29 (2H, dd, *J* = 6.0, 3.6 Hz), 4.83 (1H, dd, *J* = 7.2, 2.4 Hz), 4.70 (1H, dd, *J* = 7.5, 2.7 Hz), 2.43 (1H, dt, *J* = 13.8, 3.0 Hz), 2.24 (1H, d, *J* = 7.2 Hz), 1.94 (1H, t, *J* = 4.2 Hz), 1.76 – 1.72 (1H, m), 1.26 – 1.12 (2H), 1.15 (3H, s), 0.98 (3H, s), 0.94 (3H, s), 0.83 – 0.79 (1H, m), 0.20 (9H, s, -Si($C\underline{H}_3$)$_3$; ^{13}C NMR & APT (50 MHz, $CDCl_3$) δ 234.1 (<u>C</u>O), 159.1 (C4'), 141.0 (<u>C</u>(arene complex)-O-), 132.1 (C2' or C6'), 129.9 (C2' or C6'), 126.2 (C1'), 113.7 (C3' or C5'), 113.3 (C3' or C5'), 99.4 (<u>C</u>-*ortho* to TMS), 98.8 (<u>C</u>-*ortho* to TMS), 93.9 (<u>C</u>-TMS or C2), 93.3 (<u>C</u>-TMS or C2), 84.3 (<u>C</u>-*meta* to TMS), 82.7 (<u>C</u>-*meta* to TMS), 55.1 (C1), 55.2 (-O-$\underline{C}H_3$), 50.1 (C7), 45.5 (C4), 39.8 (C3), 30.3 (C6), 26.1 (C5), 21.6 (C8 or C9), 21.0 (C8 or C9), 9.7 (C10), -1.3 (-Si($\underline{C}H_3$)$_3$). FTIR (KBr) ν_{max} 3011, 2954, 2898, 1956, 1895, 1859 cm^{-1}.

η^6-{4-[[(1*R*,2*S*)-1,7,7-Trimethyl-2-(4-biphenyl)bicyclo[2.2.1]hept-2-yl]oxy]trimethylsilylbenzene}chromium tricarbonyl (3f) was prepared from biphenyl isoborneol **2f** as a yellow crystalline solid.



Yield: 89%; R_f: 0.13 (20:1 hexane/ether); FAB HRMS *m/z* 590.1974 (M^+), calcd for $C_{34}H_{38}O_4SiCr$; ^1H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.53 (5H), 7.50 – 7.31 (4H), 5.30 (2H, d, *J* = 7.0 Hz), 4.80 (1H, dd, *J* = 34.1, 1.9 Hz), 4.80 (1H, dd, *J* = 20.2, 2.6 Hz), 2.50 (1H, ddd, *J* = 14.2, 2.9, 4.1 Hz), 2.32 (1H, d, *J* = 14.3 Hz), 1.99 (1H, t, *J* = 4.2 Hz), 1.87 – 1.55 (1H, m), 1.38 – 1.23 (2H), 1.08 – 0.82 (1H, m), 1.19 (3H, s), 1.04 (3H, s), 0.97 (3H, s), 0.20 (9H, s, -Si(C$\underline{H}_3)_3$); ^{13}C NMR and APT (50 MHz, $CDCl_3$) δ 234.0 (C$\underline{O}$), 140.7 (C$\underline{}$(arene complex)-O-), 140.5, 140.4, 139.2 (preceding three signal correspond to C1', C4' & C7'), 129.2, 128.9, 127.5, 127.2, 127.1, 126.4, 125.5 (preceding 7 signals belong to biphenyl C-H carbons), 99.3 (C$\underline{}$-*ortho* to TMS), 98.7 (C$\underline{}$-*ortho* to TMS), 94.1 (C$\underline{}$-TMS), 93.1 (C2), 84.4 (C$\underline{}$-*meta* to TMS), 82.7 (C$\underline{}$-*meta* to TMS), 55.5 (C1), 50.4 (C7), 45.6 (C4), 39.9 (C3), 30.4 (C6), 26.1 (C5), 21.6 (C8 or C9), 21.1 (C8 or C9), 9.8 (C10), -1.3 (-Si(C$\underline{H}_3)_3$). FTIR (KBr) ν_{max} 2959, 1972, 1895, 1874 cm^{-1}.

η^6-{4-[[(*1R,2S*)-1,7,7-Trimethyl-2-ethylbicyclo[2.2.1]hept-2-yl]oxy]trimethylsilylbenzene}chromium tricarbonyl (3g) was prepared from ethyl isoborneol **2g** as a greenish yellow solid.

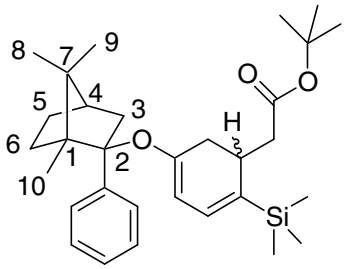


Yield: 72%; R_f: 0.55 (9:1 hexane/ethyl acetate); EI HRMS *m/z* 466.1622 (M^+), calcd for $C_{24}H_{34}O_4SiCr$ 466.1631; ^1H NMR (400 MHz, $CDCl_3$) δ 5.48 (2H, d, *J* = 6.8 Hz), 5.14 (1H, dd, *J* = 7.0, 2.2 Hz), 5.09 (1H, dd, *J* = 7.0, 2.2 Hz), 2.51 (1H, dt, *J* = 12.8, 3.7 Hz), 2.37 – 2.27 (1H, m), 1.76 – 1.58 (3H), 1.51 – 1.48 (2H), 1.35 (1H, d, *J* = 12.8 Hz), 1.11 – 1.06 (1H, m), 1.03 (3H, s), 1.00 (3H, t, *J* = 7.6 Hz), 0.92 (3H, s), 0.86 (3H, s), 0.26 (9H, s, -Si(C$\underline{H}_3)_3$); ^{13}C NMR & APT (50 MHz, $CDCl_3$) δ 234.1 (C$\underline{O}$), 141.8 (C$\underline{}$(arene complex)-O-), 99.7 (C$\underline{}$-*ortho* to TMS), 99.4 (C$\underline{}$-*ortho* to TMS), 93.6 (C$\underline{}$-TMS), 92.9 (C2), 83.1 (C$\underline{}$-*meta* to TMS), 82.8 (C$\underline{}$-*meta* to TMS), 54.1 (C1), 50.2 (C7), 45.0 (C4), 43.5 (C3), 30.0 (C6), 29.6 (C1'), 26.6 (C5), 20.9 (C8 or C9), 20.7 (C8 or C9), 12.1 (C2'), 10.5 (C10), -1.2 (-Si(C$\underline{H}_3)_3$). FTIR (KBr) ν_{max} 2958, 1985, 1872, 1865 cm^{-1}.

General Procedure for Nucleophilic Addition/Electrophilic Addition/Demetallation Sequence:

To a solution of diisopropylamine (1.7 mL, 12.5 mmol, 5 equiv) in anhydrous THF (12.5 mL) at 0 ºC was added dropwise *n*-butyllithium (1.6 M in hexanes; 5.0 mL, 12.5 mmol, 5 equiv). After 15 min, the resulting LDA solution was cooled to -78 ºC and a solution of *tert*-butyl acetate (1.9 mL, 2.5 mmol, 5 equiv) in THF (12.5 mL) was added dropwise. After an additional 30 min a solution of the arene tricarbonyl chromium complex (2.5 mmol, 1 equiv) in 12.5 mL of THF was added, followed immediately by the addition of anhydrous HMPA (5.4 mL, 31 mmol, 12.5 equiv). The resulting heterogeneous, yellow reaction mixture was warmed to -60 ºC and maintained at this temperature for the duration of the reaction. After 4 h trifluoroacetic acid (5.2 mL, 67.5 mmol, 27 equiv) was added in one portion and the reaction mixture immediately became a deep red color. After 0.5 h the reaction mixture was removed from the cooling bath and diluted with concentrated aqueous ammonia (5 mL). Finally, after an additional 0.5 h the now heterogeneous green reaction mixture was diluted with additional aqueous concentrated ammonia and extracted with ether. The combined ether extracts were washed with water, dried ($MgSO_4$), then filtered and concentrated *in vacuo,* usually affording green colored oil. The product was then purified by column chromatography using hexane/ethyl ether eluent system.

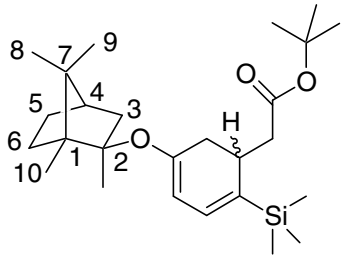
***tert*-Butyl [5-[[(1*R*,2*S*)-1,7,7-trimethyl-2-phenylbicyclo[2.2.1]hept-2-yl]oxy]2-trimethylsilylcyclohexa-2,4-dien-1-yl] acetate (5a)** was prepared by nucleophilic addition of *tert*-butyl lithioacetate to complex **3a** and purified by flash column chromatography (20:1 hexane/ether).



Yield: 72%; R_f: 0.48 (20:1 hexane/ether); Data for major diastereomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 – 7.49 (1H, m), 7.40 – 7.20 (4H), 5.91 (1H, d, *J* = 5.7 Hz), 4.17 (1H, dd, *J* = 5.7, 2.2 Hz), 2.75 – 2.64 (1H, m), 2.48 (1H, dt, *J* = 14.4, 3.6 Hz), 2.37 (1H, dd, *J* = 16.6, 6.7

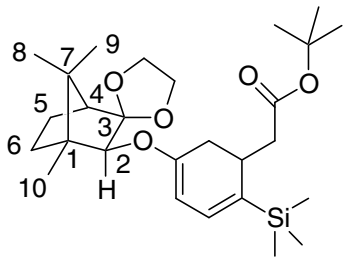
Hz), 2.24 (1H, dd, *J* = 14.5, 12.0 Hz), 2.17 (1H, d, *J* = 14.3 Hz), 2.07 (1H, d, *J* = 16.6 Hz), 1.92 – 1.82 (2H), 1.83 – 1.67 (1H, m), 1.56 (9H, s), 1.56 – 1.42 (1H, m), 1.36 – 1.08 (2H), 1.07 (3H, s), 0.92 (2x3H, s), 0.01 (9H, s, -Si($C\underline{H}_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.6 (-$\underline{C}OOC(CH_3)_3$), 150.7 (C1'), 141.6 (C1"), 133.6 (C3'), 130.3 (C4'), 128.4, 127.7, 127.1, 126.7, 125.6 (preceding five signals correspond to C-H aromatic carbons), 99.9 (C2'), 89.8 (C2), 80.3 (C6'), 54.6 (C1), 50.4 (C7), 45.5 (C4), 40.4 (C3), 36.1 (C5'-$\underline{C}H_2$-COO-), 32.5 (C5), 31.7 (C5'), 30.2 (C6), 28.3 (-COOC($\underline{C}H_3)_3$), 26.4 (-COO$\underline{C}(CH_3)_3$), 21.6 (C8 or C9), 21.2 (C8 or C9), 10.1 (C10), -1.4 (-Si($\underline{C}H_3)_3$). The diastereomer ratio from ^{1}H NMR = **21:1**. The major isomer was determined to be ***S*** from optical rotation and CD spectrum of the derived cyclohexenone.

***tert*-Butyl [5-[[(1*R*,2*S*)-1,2,7,7-tetramethylbicyclo[2.2.1]hept-2-yl]oxy]2-trimethylsilylcyclohexa-2,4-dien-1-yl] acetate (5b)** was prepared by nucleophilic addition of *tert*-butyl lithioacetate to complex **3b** and purified by flash column chromatography (20:1 hexane/ether).



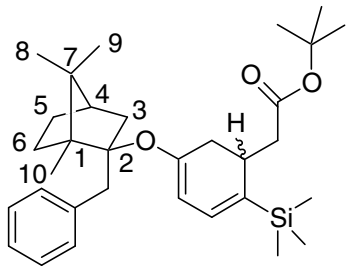
Yield: 85%; R_f: 0.58 (20:1 hexane/ether); partial data for major diastereomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.18 (1H, d, *J* = 5.8 Hz), 4.89 (1H, dd, *J* = 2.0, 5.8 Hz), 2.80 – 2.25 (1H, m), 2.05 – 1.94 (3H), 1.80 – 1.60 (3H), 1.46 (9H, s), 0.09 (9H, s, -Si($C\underline{H}_3)_3$). Partial data for minor diastereomer: δ 6.17 (1H, d, *J* = 6.0 Hz), 1.44 (9H, s). The diastereomer ratio from ^{1}H NMR = **1.2:1**. The major isomer was determined to be ***S*** from optical rotation and CD spectrum of the derived cyclohexenone.

***tert*-Butyl [5-[[[Spiro[(1*R*,2*S*)-1,7,7-trimethylbicyclo[2.2.1]heptane-3,2'-[1,3]dioxalan]-2-yl]oxy]2-trimethylsilylcyclohexa-2,4-dien-1-yl] acetate (5c)** was prepared by nucleophilic addition of *tert*-butyl lithioacetate to complex **3c** and purified by flash column chromatography (20:1 hexane/ether).



Yield: 65%; R_f: 0.71 (20:1 hexane/ether); ^{1}H NMR (300 MHz, $CDCl_3$) Partial data for major diastereomer δ 6.18 (1H, d, *J* = 5.8 Hz), 4.89 (1H, dd, *J* = 5.8, 2.0 Hz), 4.02 – 3.71 (4H), 3.79 (1H, s), 2.80 – 2.73 (1H, m), 1.45 (9H, s), 0.88 (3H, s), 0.84 (3H, s), 0.09 (9H, s, (-Si($\underline{C}H_3)_3$). Partial data for Minor diastereomer: δ 6.18 (1H, d, *J* = 6.0 Hz), 1.47 (9H, s); The diastereomer ratio from ^{1}H NMR = **70:30.** The major isomer was determined to be ***R*** from optical rotation of the corresponding cyclohexenone.

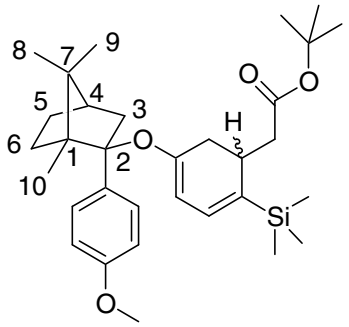
***tert*-Butyl [5-[[(1*R*,2*S*)-1,7,7-trimethyl-2-benzylbicyclo[2.2.1]hept-2-yl]oxy]2-trimethylsilylcyclohexa-2,4-dien-1-yl] acetate (5d)** was prepared by nucleophilic addition of *tert*-butyl lithioacetate to complex **3d,** and purified by flash column chromatography (20:1 hexane/ether).



Yield: 72%; R_f: 0.48 (20:1 hexane/ether); ^{1}H NMR (200 MHz, $CDCl_3$) Partial data for major diastereomer: δ 6.21 (1H, d, *J* = 5.9 Hz), 5.14 (1H, dd, *J* = 2.1, 5.9 Hz), 3.90 (1H, d, *J* = 15.0 Hz), 0.94 (3H, s), 0.80 (3H, s), 0.34 (3H, s), 1.44 (9H, s), 0.13 (9H, s, -Si(C$\underline{H}_3)_3$); Partial data for minor diastereomer: δ 6.20 (1H, d, *J* = 6.0 Hz), 5.07 (1H, dd, *J* = 2.0, 6.0 Hz), 3.84 (1H, d, *J* = 14.8 Hz), 1.50 (9H, s), 0.83 (3H, s), 0.79 (3H, s), 0.40 (3H, s), 0.12 (9H, s, -Si(C$\underline{H}_3)_3$). The diastereomer ratio from ^{1}H NMR = **38:62**.The major isomer was determined to be ***R*** from optical rotation and CD spectrum of the corresponding cyclohexenone.

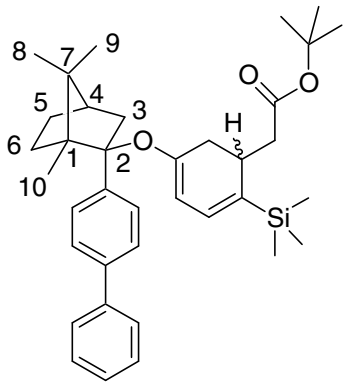
***tert*-Butyl [5-[[(1*R*,2*S*)-1,7,7-trimethyl-[4-methoxyphenyl]bicyclo[2.2.1]hept-2-yl]oxy]2-trimethylsilylcyclohexa-2,4-dien-1-yl] acetate (5e)** was prepared by nucleophilic addition

of *tert*-butyl lithioacetate to complex **3e,** and purified by flash column chromatography (20:1 hexane/ethyl acetate).



Yield: 87%; R_f: 0.20 (20:1 hexane/ethyl acetate); Data for major diastereomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 – 7.30 (1H, m), 7.23 – 7.18 (1H, m), 6.88 – 6.77 (2H), 6.00 (1H, d, *J* = 6.3 Hz), 4.12 (1H, dd, *J* = 2.3, 6.2 Hz), 3.79 (3H, s), 2.94 – 2.90 (1H, m), 2.45 – 2.30 (3H), 2.17 – 2.07 (2H), 1.83 (1H, t, *J* = 4.1 Hz), 1.78 – 1.62 (1H, m), 1.47 (9H, s), 1.26 – 1.09 (4H), 1.05 (3H, s), 0.92 (3H, s), 0.90 (3H, s), 0.04 (9H, s, -Si($C\underline{H}_3$)$_3$). Partial data for minor diastereomer: δ 5.95 (1H, d, J = 6.3 Hz), 3.80 (3H, s).; The diastereomer ratio from ^{1}H NMR = **90:10**. The major isomer was determined to be ***S*** from optical rotation and CD spectrum of the corresponding cyclohexenone.

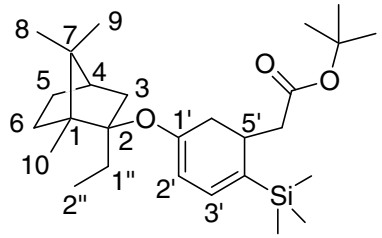
***tert*-Butyl [5-[[(1*R*,2*S*)-1,7,7-trimethyl-2-(1-biphenyl)bicyclo[2.2.1]hept-2-yl]oxy]2-trimethylsilylcyclohexa-2,4-dien-1-yl] acetate (5f)** was prepared by nucleophilic addition of *tert*-butyl lithioacetate to complex **3f,** and purified by flash column chromatography (20:1 hexane/ethyl acetate).



Yield: 82%; R_f: 0.53 (14:1 hexane/ethyl acetate); ^{1}H NMR (600 MHz, $CDCl_3$) Major diastereomer: δ 7.64 – 7.55 (5H), 7.47 – 7.40 (3H), 7.33 (1H, t, *J* = 7.5 Hz), 5.93 (1H, d, *J* =

6.0 Hz), 4.23 (1H, dd, *J* = 5.7, 2.1 Hz), 2.72 – 2.69 (1H, m), 2.52 (1H, dt, *J* = 13.8, 3.9 Hz), 2.41 – 2.37 (1H, m), 2.29 – 2.24 (1H, m), 2.20 (1H, d, *J* = 14.4 Hz), 2.09 (1H, dd, *J* = 16.5, 1.5 Hz), 1.90 – 1.86 (2H), 1.80 – 1.75 (1H, m), 1.58 (9H, s), 1.35 – 1.31 (1H, m), 1.23 – 1.14 (1H, m), 1.09 (3H, s), 1.02 – 0.98 (1H, m), 0.96 (3H, s), 0.94 (3H, s), 0.02 (9H, s, -Si($C\underline{H}_3$)$_3$). Minor diastereomer: δ 5.86 (1H, d, *J* = 6.0 Hz), 4.26 (1H, dd, *J* = 6.3, 2.1 Hz); The diastereomer ratio from ^{1}H NMR = **90:10**. The major isomer was determined to be ***S*** from optical rotation of the corresponding cyclohexenone.

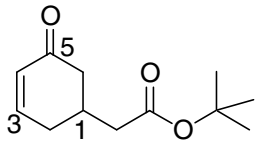
***tert*-Butyl [5-[[(1*R*,2*S*)-1,7,7-trimethyl-2-(1-ethyl)bicyclo[2.2.1]hept-2-yl]oxy]2-trimethylsilylcyclohexa-2,4-dien-1-yl] acetate (5g)** was prepared by nucleophilic addition of *tert*-butyl lithioacetate to complex **3g** and purified by flash column chromatography (20:1 hexane/ethyl acetate).



Yield: 81%; R_f: 0.49 (20:1 hexane/ethyl acetate); Data for major diastereomer: ^{1}H NMR (400 MHz, C_6D_6) δ 6.25 (1H, d, *J* = 6.0 Hz), 4.96 (1H, dd, *J* = 5.6, 2.0 Hz), 3.08 (1H, tt, *J* = 9.4, 2.4 Hz), 2.78 – 2.71 (2H), 2.65 – 2.60 (1H, m), 2.55 – 2.40 (1H, m), 2.39 – 2.20 (2H), 1.70 – 1.51 (2H), 1.60 – 1.28 (4H), 1.42 (9H, s, -COOC($C\underline{H}_3$)$_3$), 1.16 (3H, s), 1.10 – 1.01 (2H), 1.08 (3H, s), 0.95 – 0.81 (2H), 0.84 (3H, s), 0.15 (9H,s, -Si($C\underline{H}_3$)$_3$)); ^{13}C NMR & APT (50 MHz, C_6D_6) δ 171.7 (-$\underline{C}$OOC(CH_3)$_3$), 151.9 (C1'), 134.3 (C3'), 130.2 (C4'), 98.2 (C2'), 89.1 (C2), 79.5 (C6'), 53.6 (C1), 50.5 (C7), 45.5 (C4), 43.7 (C3), 36.3 (C5'-$\underline{C}H_2$-COO-), 32.6 (C1''), 32.6 (C5'), 30.5 (C6), 28.2 (-COOC($\underline{C}H_3$)$_3$), 27.8 (-COO$\underline{C}$(CH_3)$_3$), 27.2 (C5), 21.7 (C8 or C9), 21.0 (C8 or C9), 12.8 (C2''), 10.3 (C10), -1.0 (-Si($\underline{C}H_3$)$_3$). The diastereomer ratio from ^{1}H NMR = **2:1**. The major isomer was determined to be ***S*** from the optical rotation of the corresponding cyclohexenone.

***tert*-Butyl (5-oxo-cyclohex-3-enyl) acetate (6)** A solution of the cyclohexadienol ether **5** (1 equiv) from each nucleophilic addition, and *para*-toluenesulfonic acid monohydrate (2 equiv)

in diethyl ether was stirred at room temperature until tlc indicated complete disappearance of the dienol ether (approximately 4 h). The reaction mixture was then diluted with saturated aqueous $NaHCO_3$ solution and extracted three times with diethyl ether. The combined ether extracts were washed with brine, dried (Na_2SO_4), and solvent removed *in vacuo* to yield an oil. Purification by preparative tlc afforded the enone as a colorless oil. The chiral auxiliaries were recovered without changes in most cases.



R_f: 0.34 (3:1 hexane/ethyl acetate); [Literature[6]: $[\alpha]^{25}_D = +37.2$ ° (c = 10, $CHCl_3$) for the *S* isomer]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.97 (1H, ddd, J = 2.7, 5.3, 10.1 Hz), 6.04 (1H, d, J = 10.1 Hz), 2.62 – 2.46 (3H), 2.33 – 2.07 (4H), 1.46 (9H, s, -COOC($C\underline{H}_3$)$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.8 (C5), 170.9 (-$\underline{C}$OOC(CH_3)$_3$), 149.3 (C3), 129.7 (C4), 80.5 (-COO$\underline{C}$(CH_3)$_3$), 43.8 (-$\underline{C}H_2$-COO-), 41.2 (C6), 32.0 (C5), 31.5 (C2), 28.1 (-COOC($\underline{C}H_3$)$_3$); FTIR (KBr, cm-1) 3039, 2980, 2934, 1729, 1690, 1624 cm^{-1}.

References

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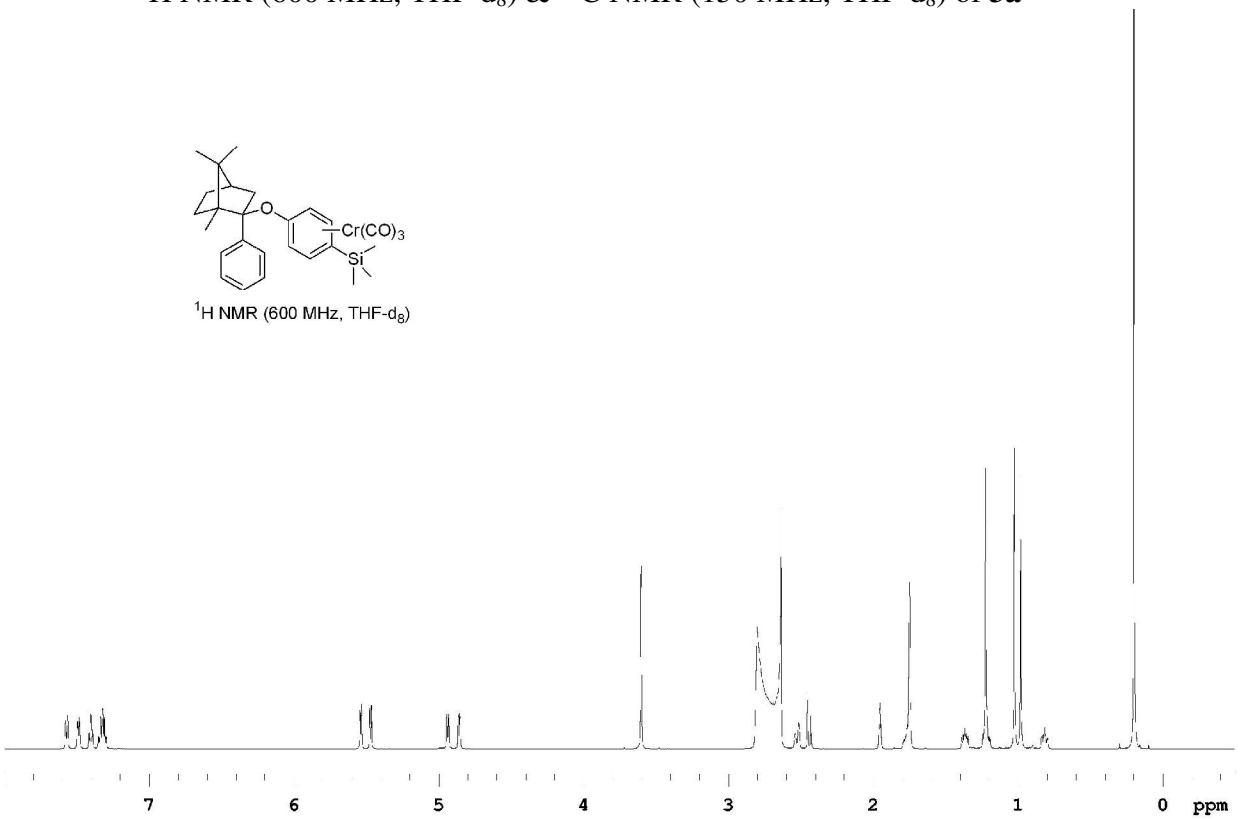
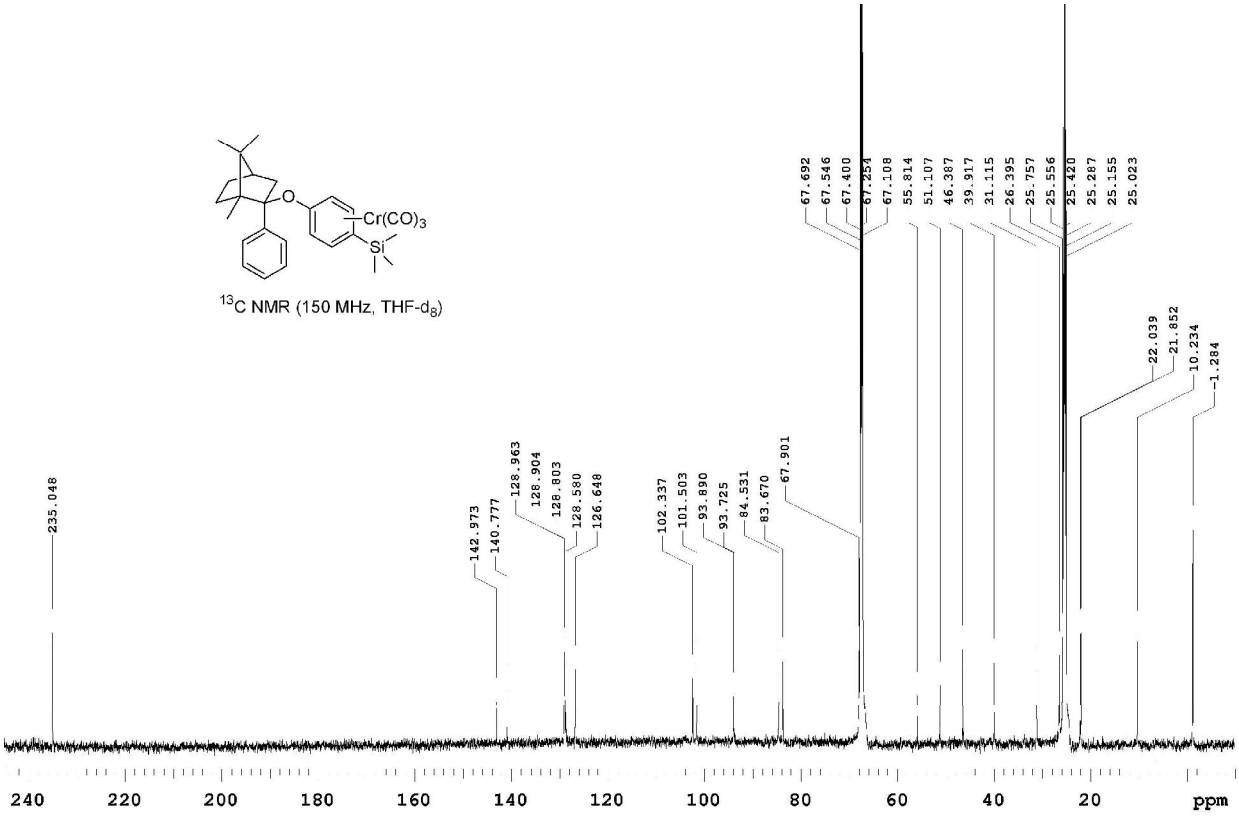
[2] Oppolzer, W.; Chapuis, C.; Dupuis, D.; Guo, M. *Helv. Chim. Act.* **1985**, *68*, 2100-2114.
[3] Mahaffy, C. A. L.; Pauson, P. L. *Inorganic Syntheses* **1979**, *19*, 154-158.
[4] Moerlein, S. M. *J. Organomet. Chem.* **1987**, *319*, 29-39.
[5] Fleming, I.; Woodward, R. B. *J. Chem. Soc. (C)* **1968**, 1289-1291.
[6] Dudones, J. D.; Pearson, A. J. *Tetrahedron Lett.* **2000**, *41*, 8037-8040.

^{1}H NMR, ^{13}C NMR , ^{1}H-^{1}H COSY, ^{1}H-^{13}C HMQC, NOE & ^{13}C NMR assignments

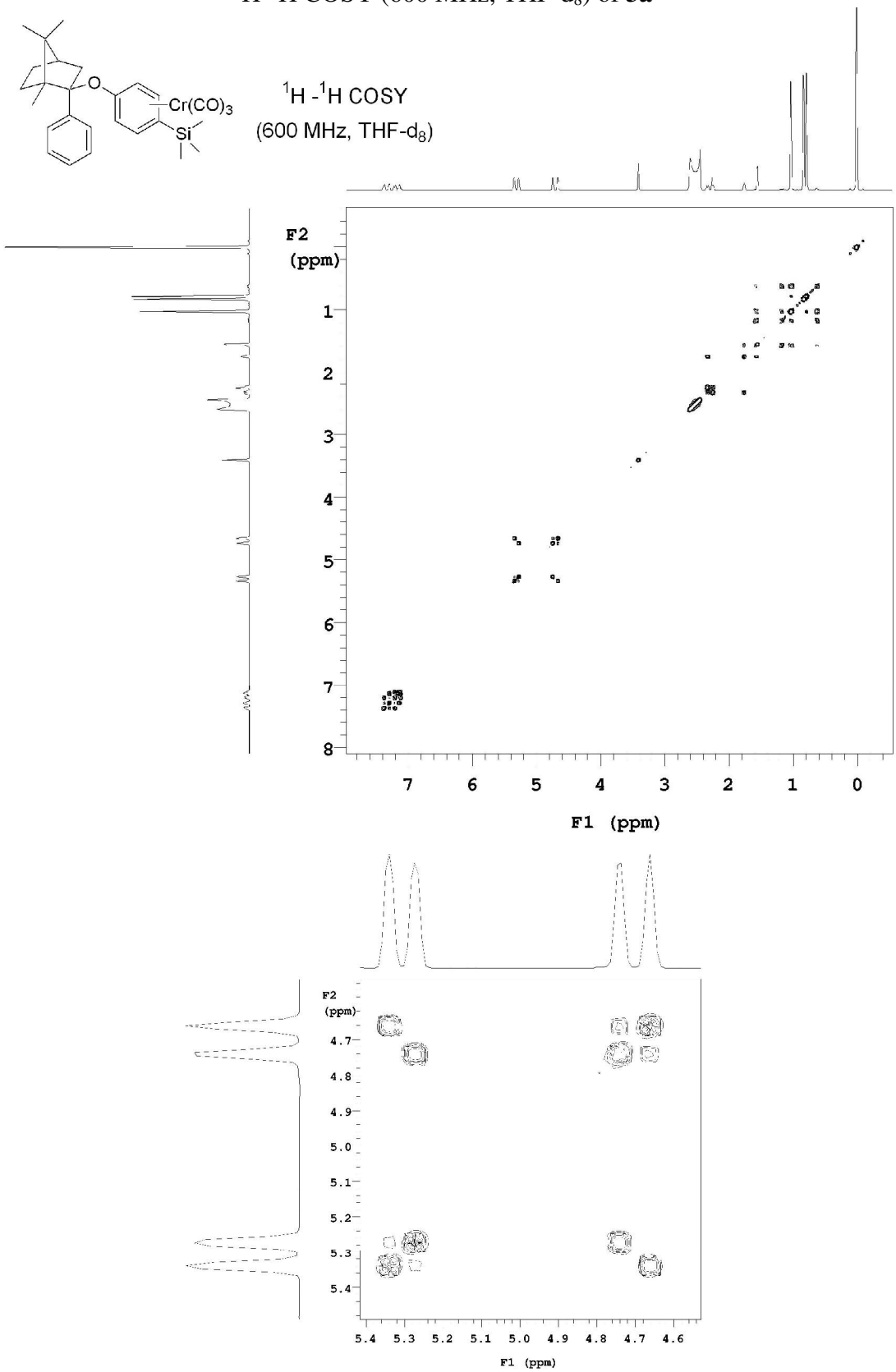
Of Complexes **3a**, **3b**, **3c**, **3d**, **3e** and **3f** & OTHER NMR SPECTRA

^{1}H NMR (600 MHz, THF-d_8) & ^{13}C NMR (150 MHz, THF-d_8) of **3a**

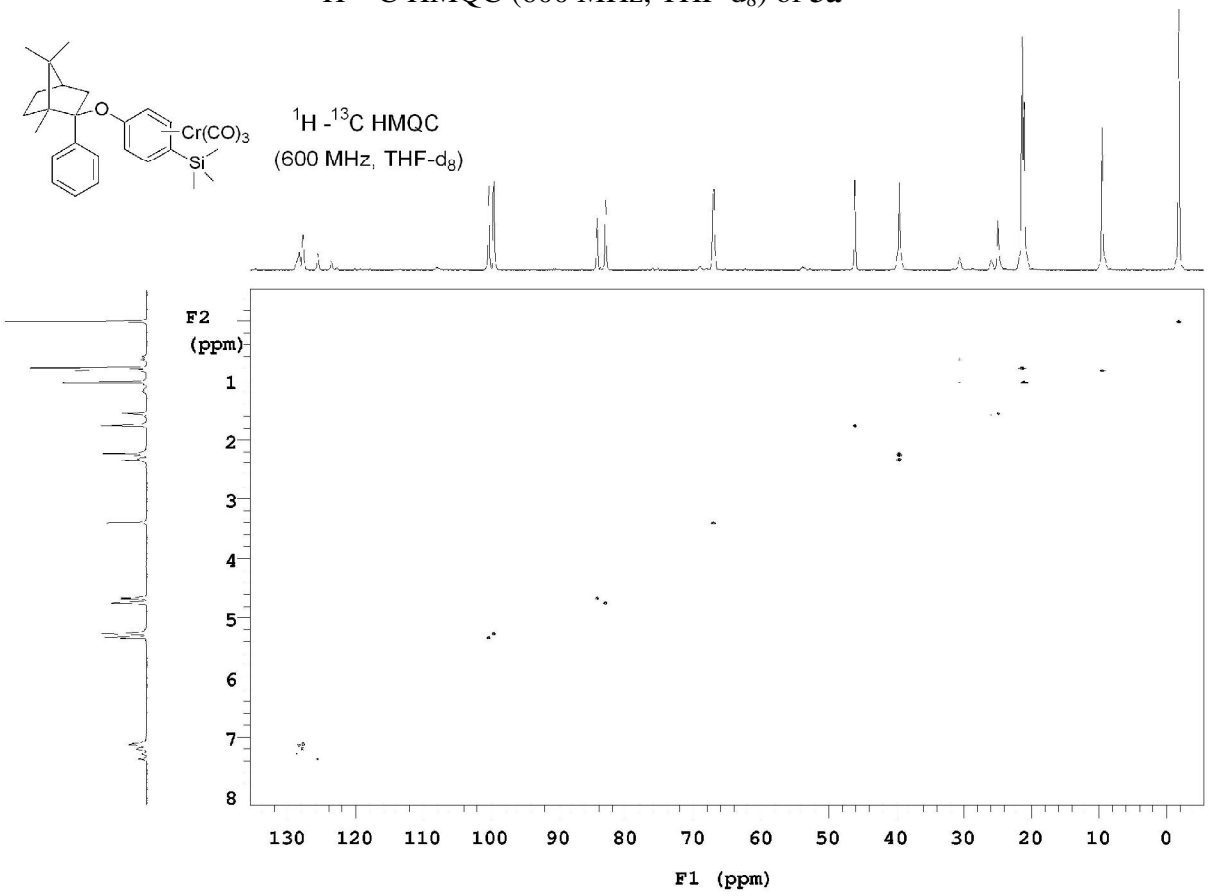


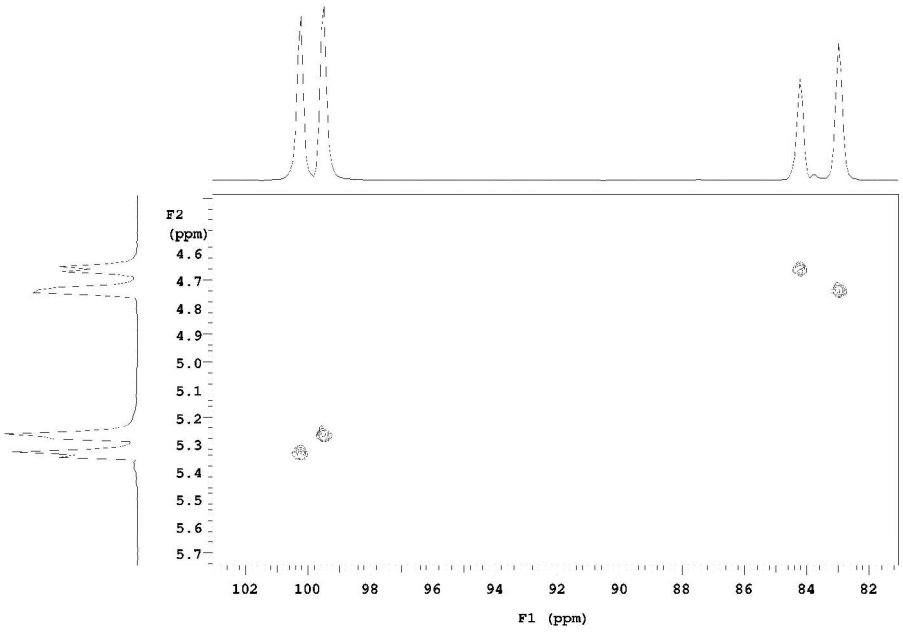


^{1}H-^{1}H COSY (600 MHz, THF-d_8) of **3a**



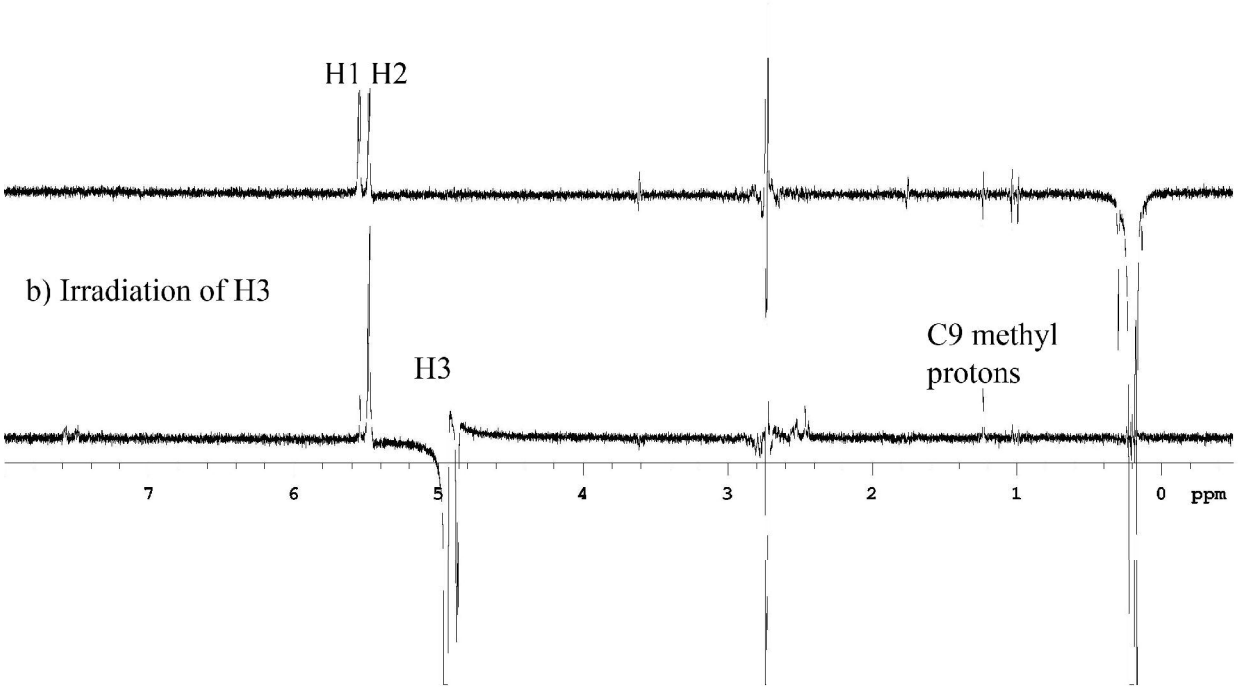
^{1}H-^{13}C HMQC (600 MHz, THF-d_8) of **3a**



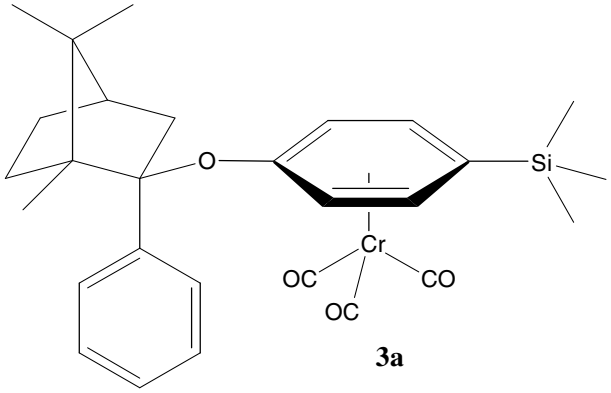


^{1}H NOE (600 MHz, THF-d_8) of **3a**

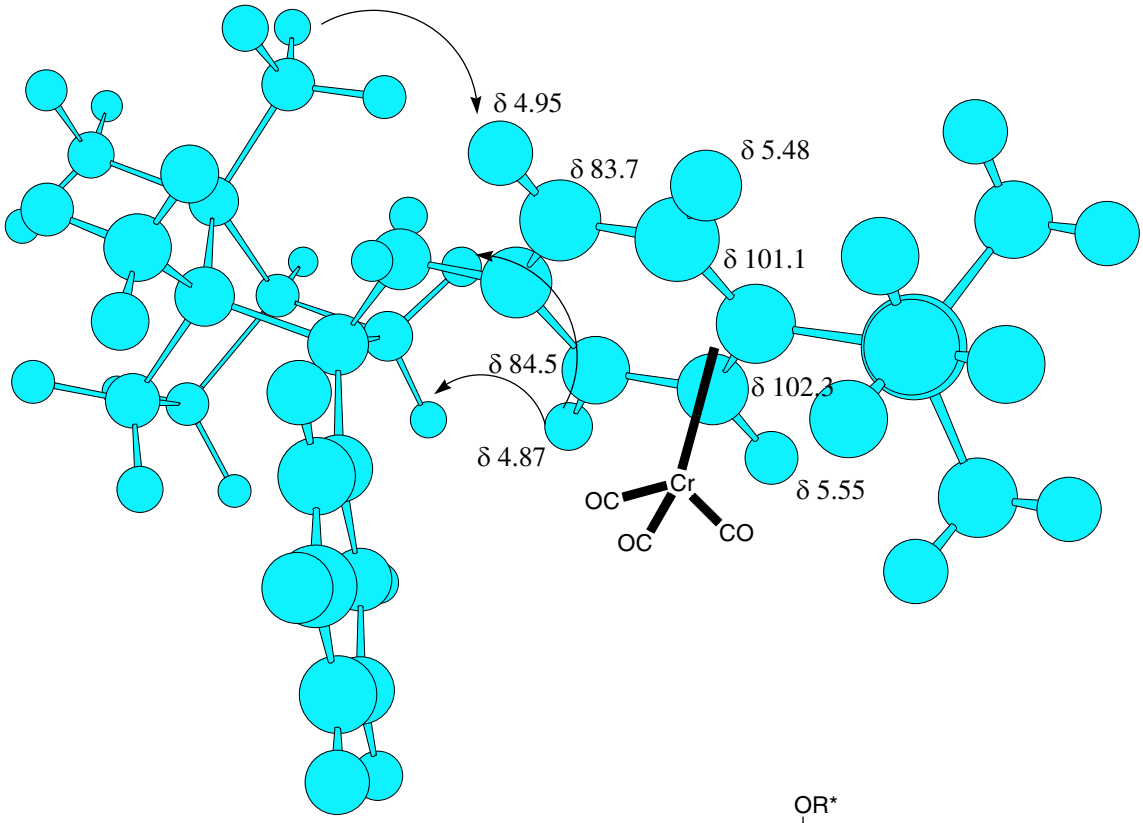
a) Irradiation of -TMS methyl protons

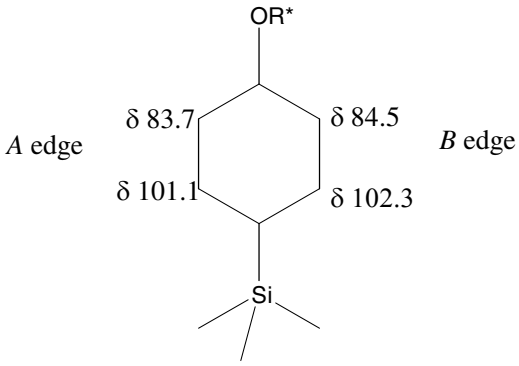


Representation of NOEs of complex **3a** (600 MHz, THF-d_8) and final assignment of arene carbons:

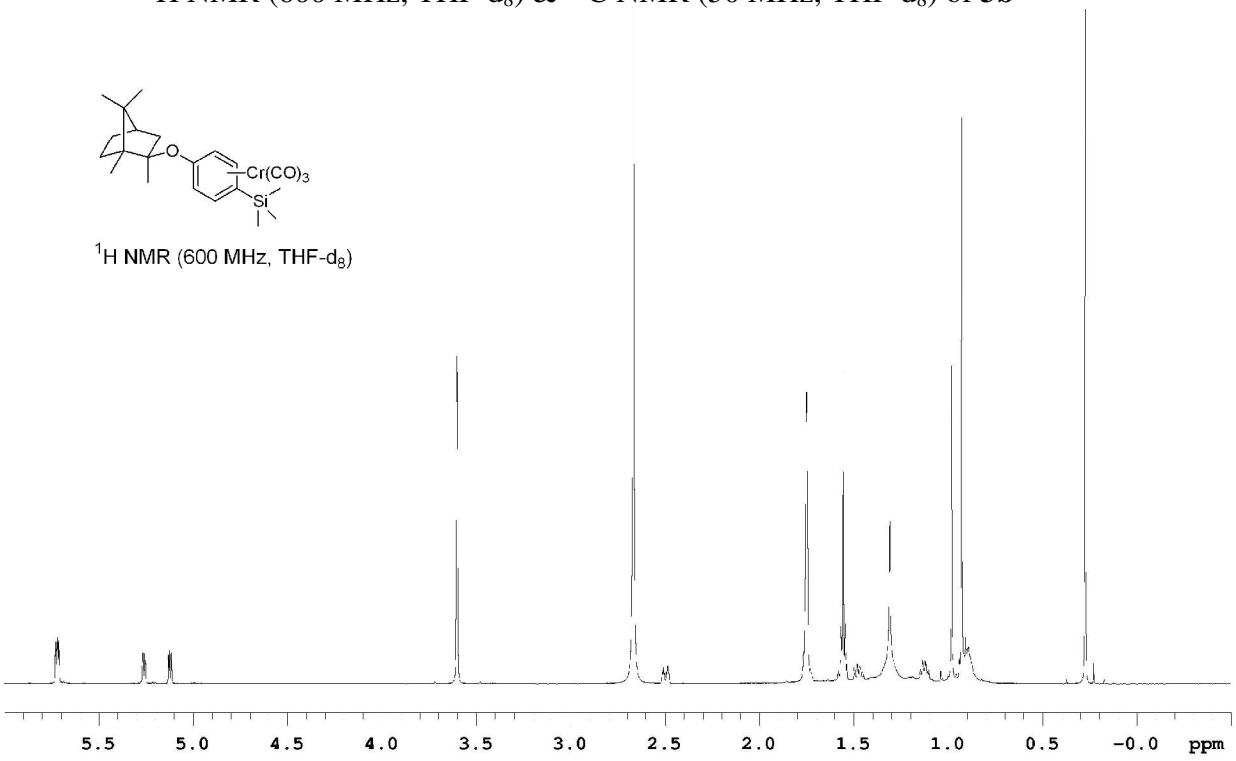


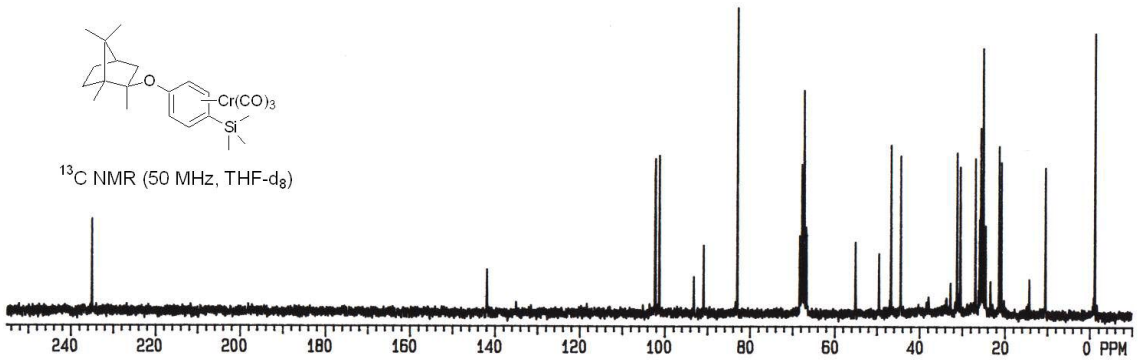
3a

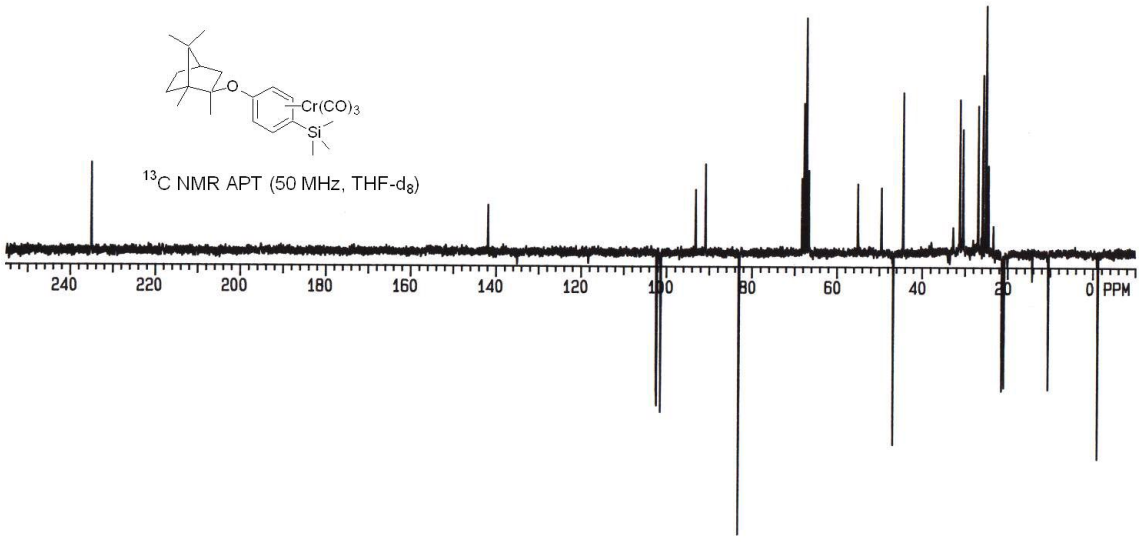




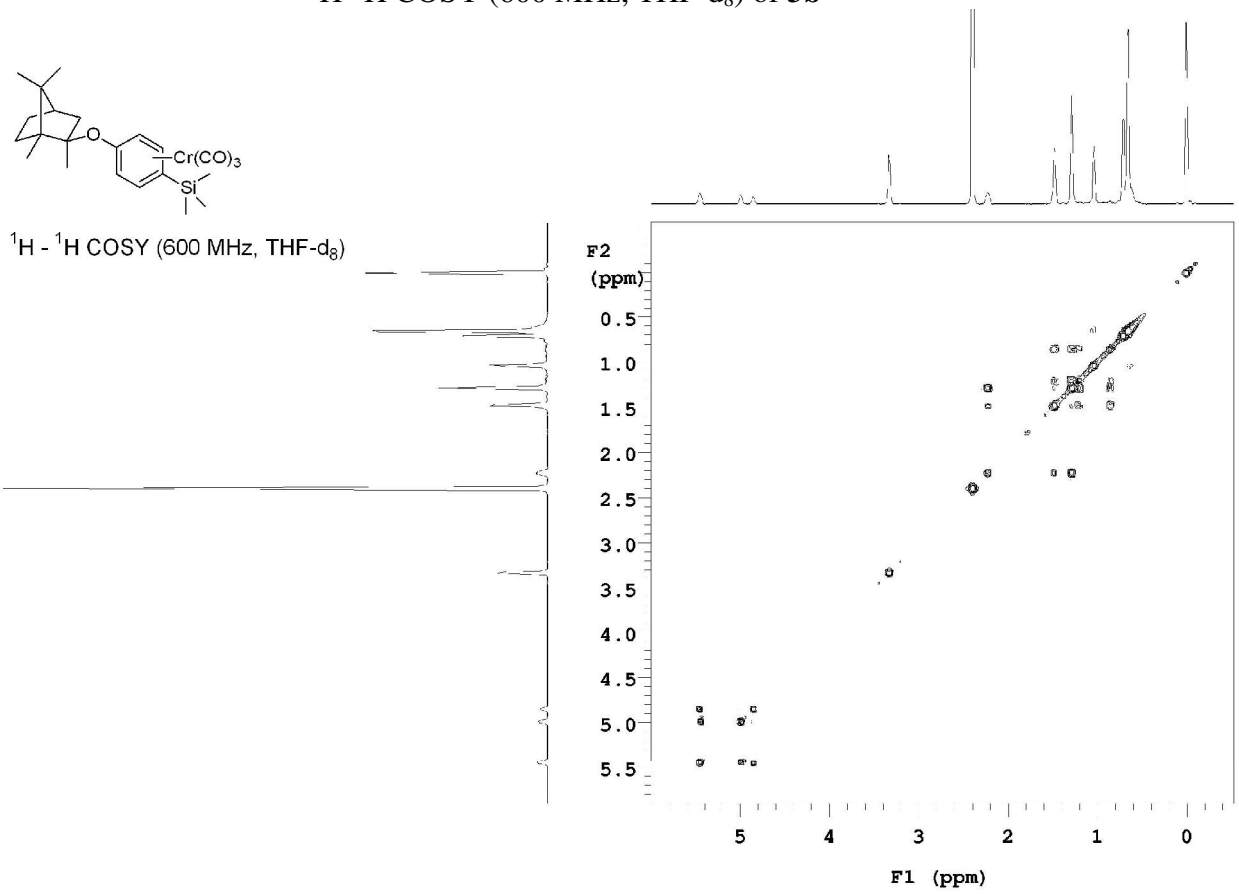
^{1}H NMR (600 MHz, THF-d_8) & ^{13}C NMR (50 MHz, THF-d_8) of **3b**

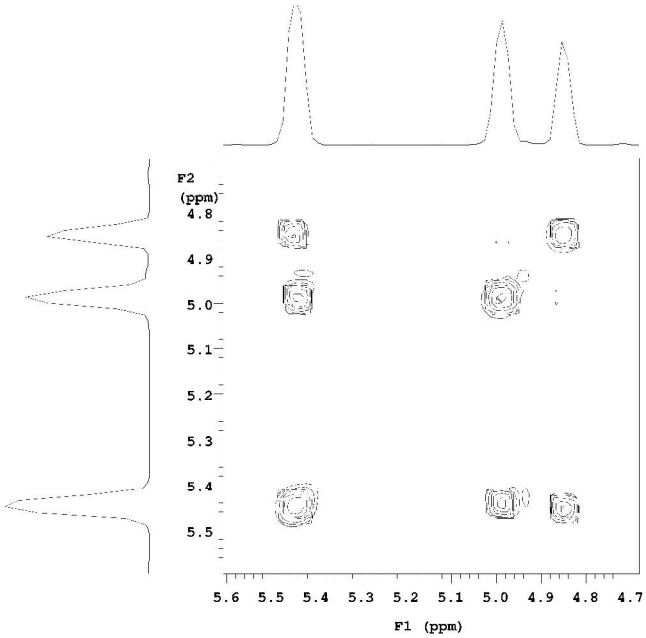




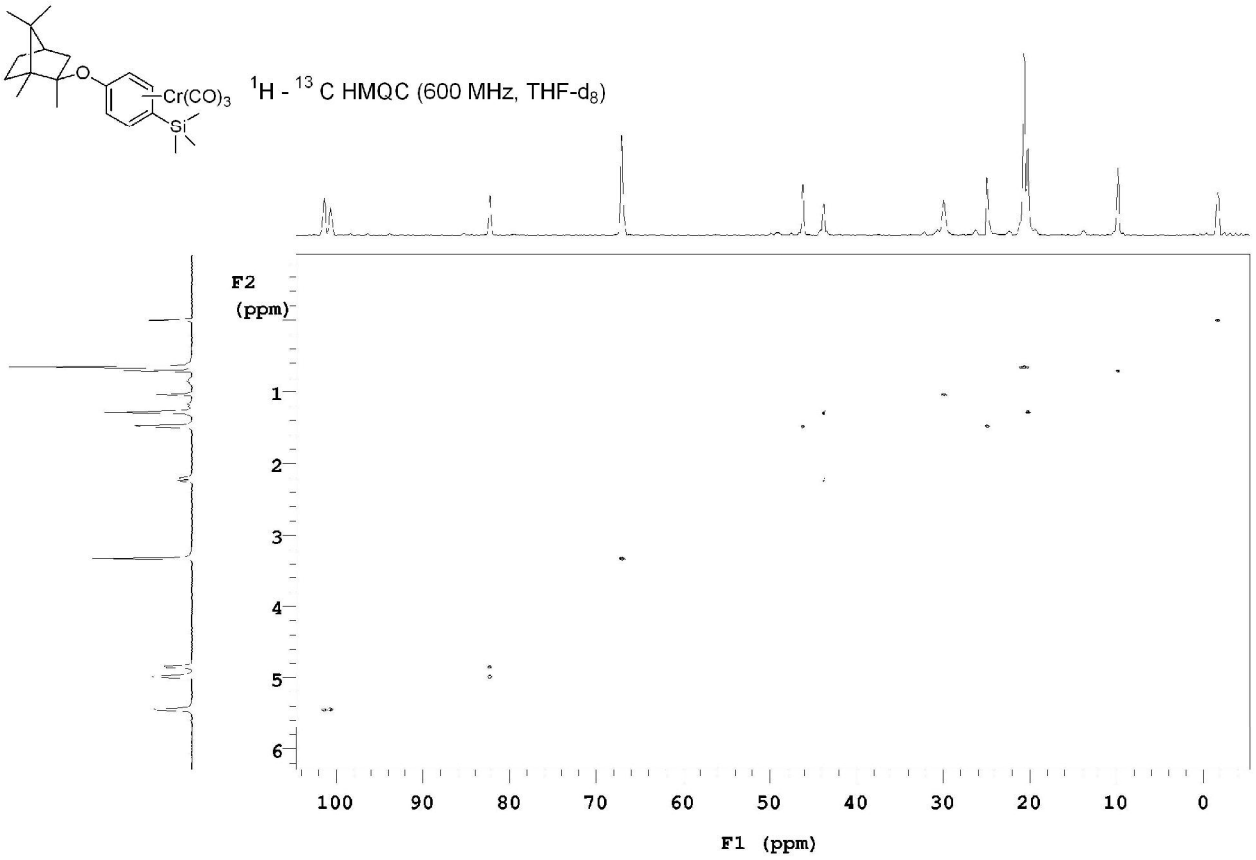


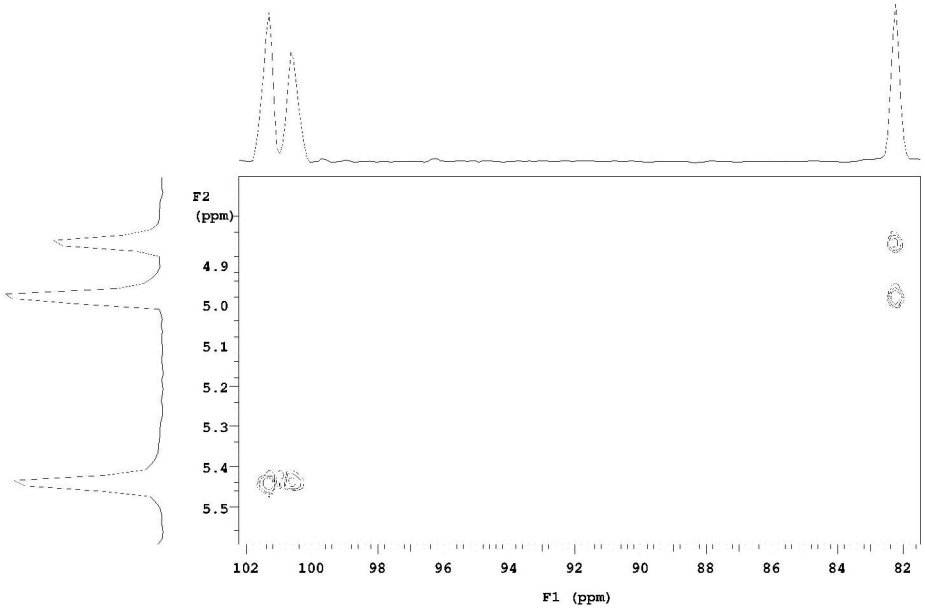
^{1}H-^{1}H COSY (600 MHz, THF-d_8) of **3b**



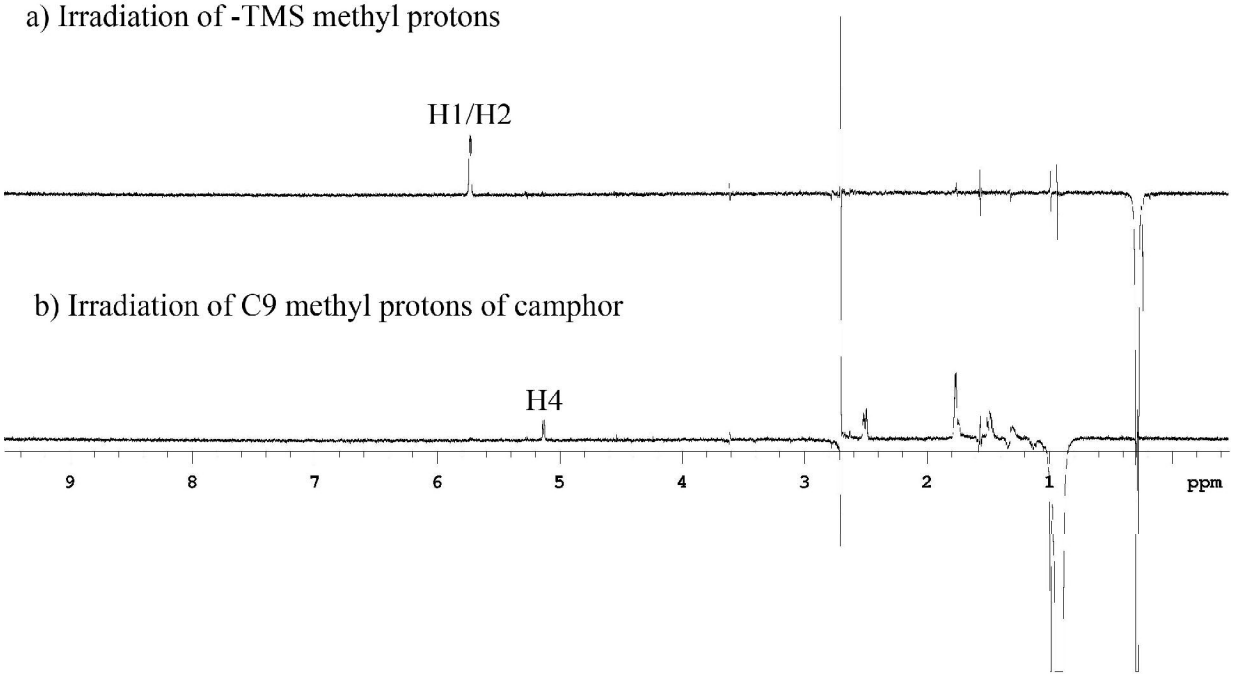


^{1}H-^{13}C HMQC (600 MHz, THF-d_8) of **3b**

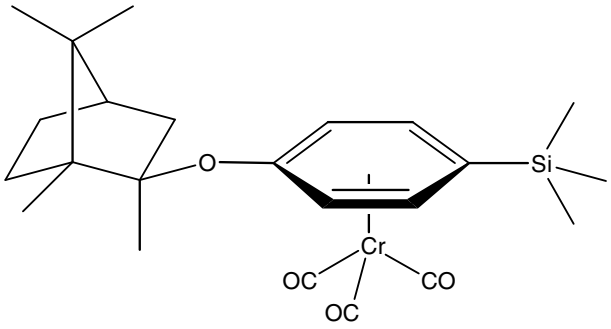




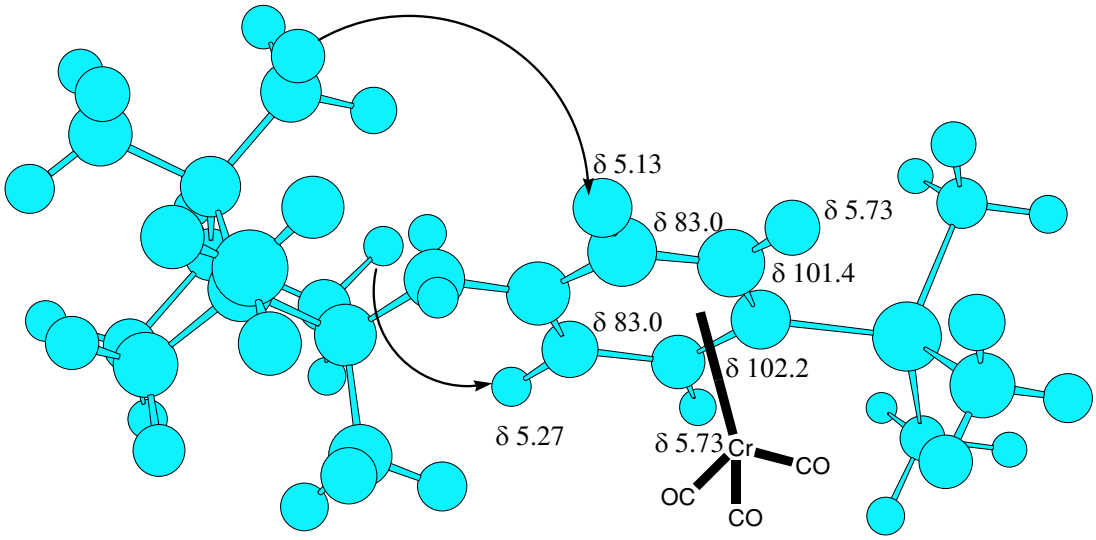
^{1}H NOE (600 MHz, THF-d_8) of **3b**

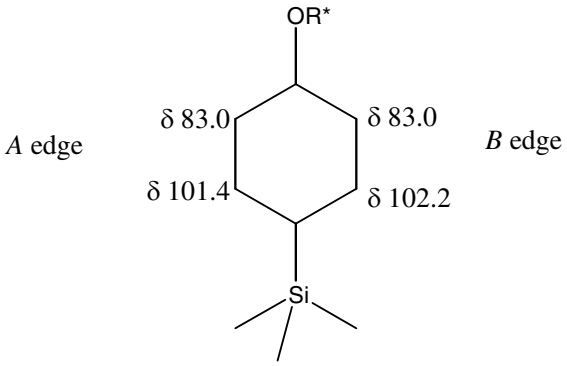


Representation of NOEs of complex **3b** (600 MHz, THF-d_8) and final assignment of arene carbons:



3b

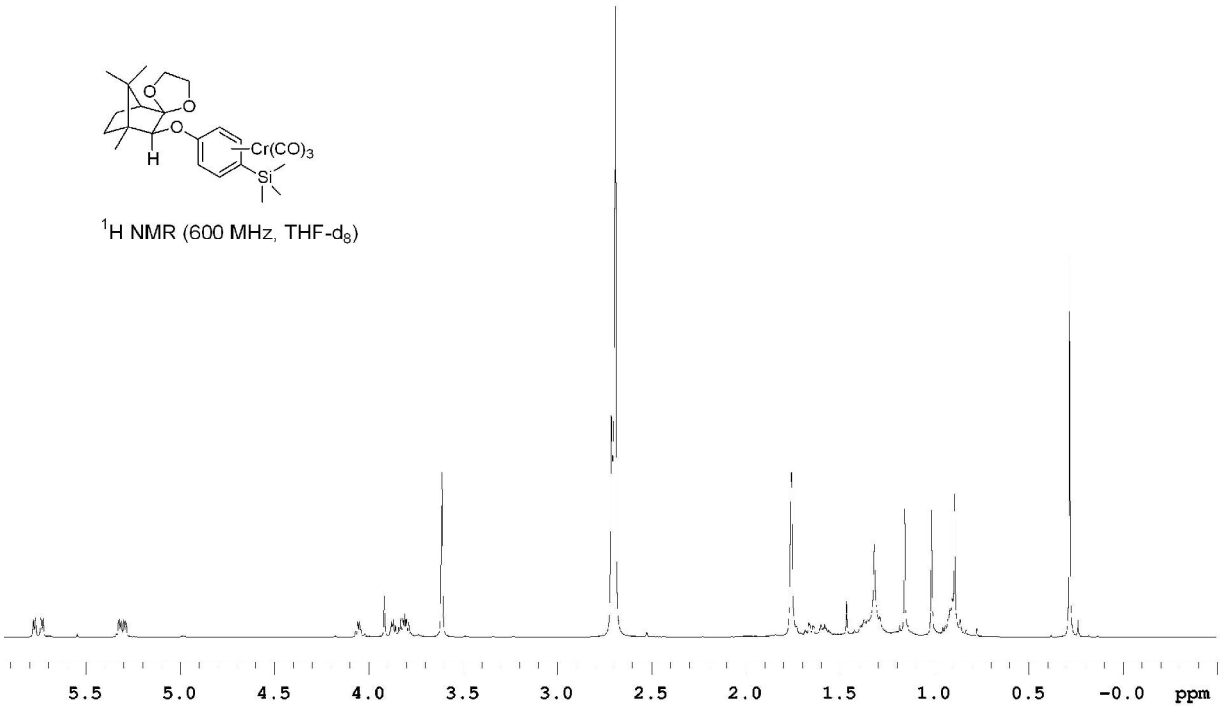


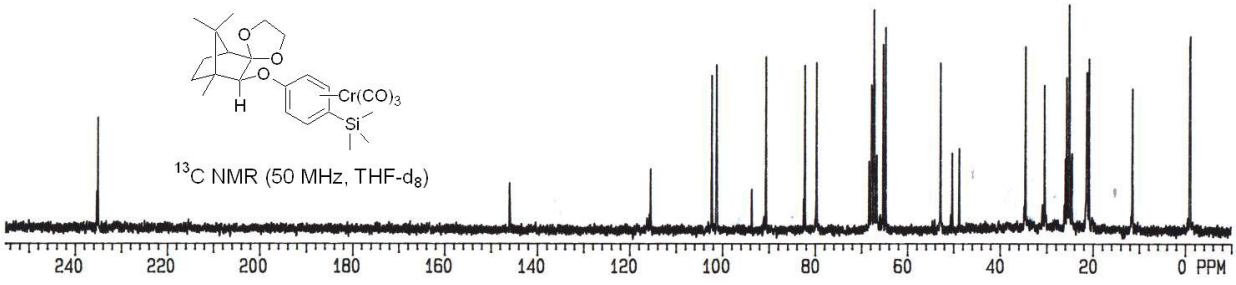


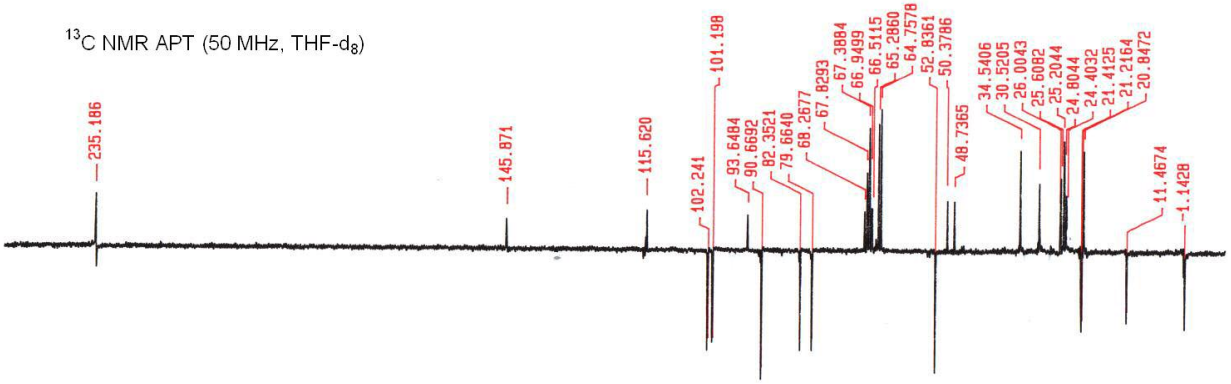
A edge

B edge

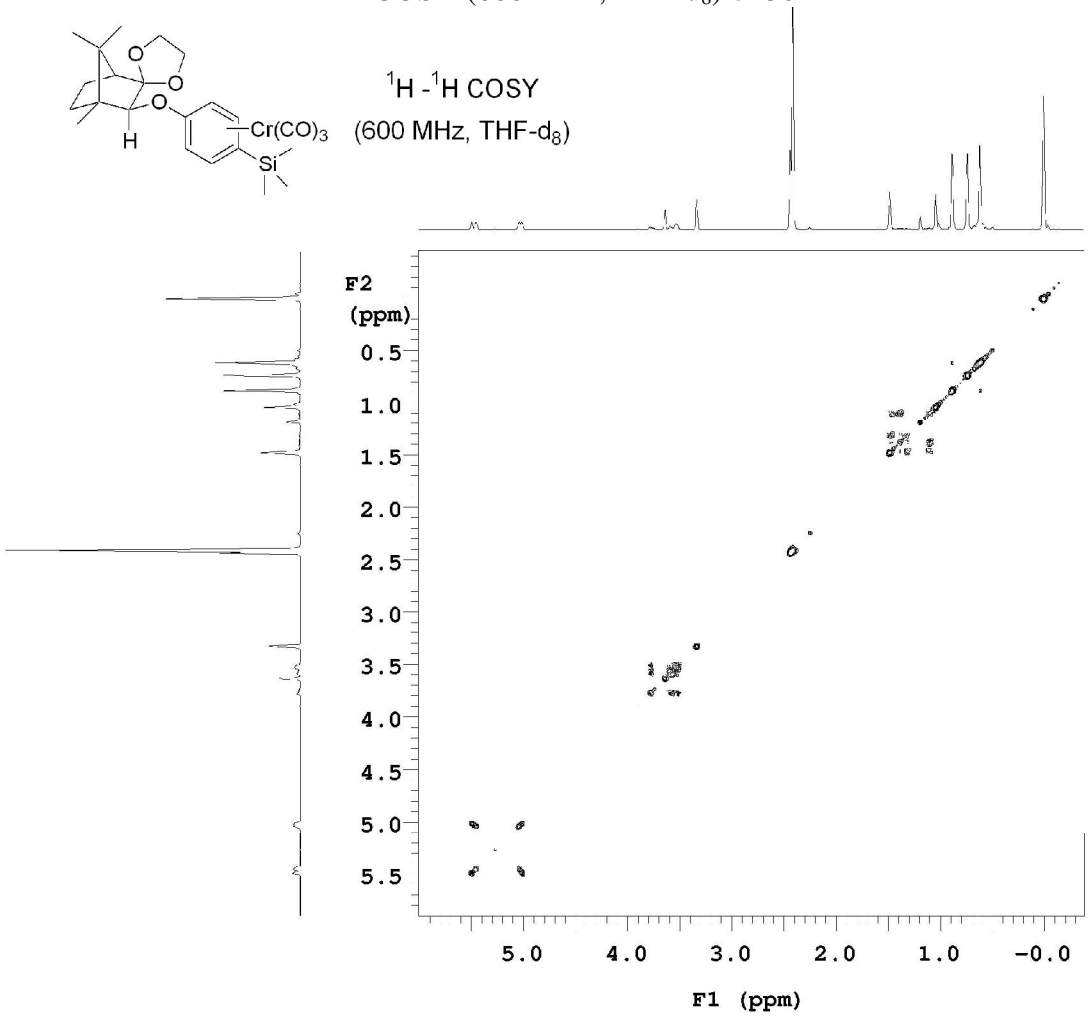
^{1}H NMR (600 MHz, THF-d_8) & ^{13}C NMR (50 MHz, THF-d_8) of **3c**

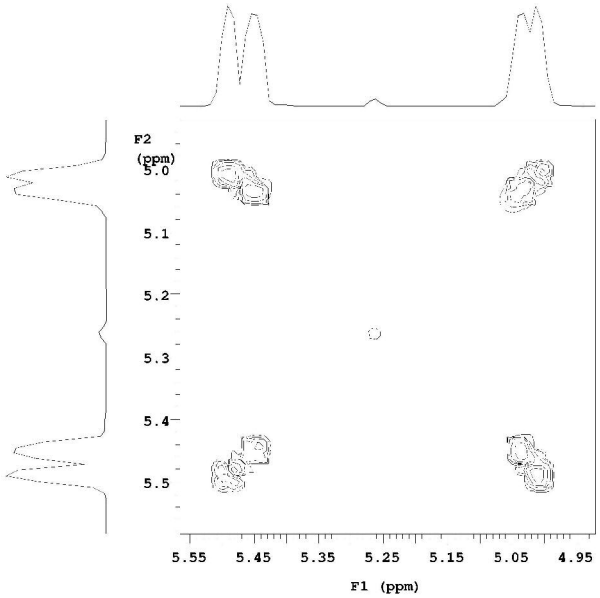




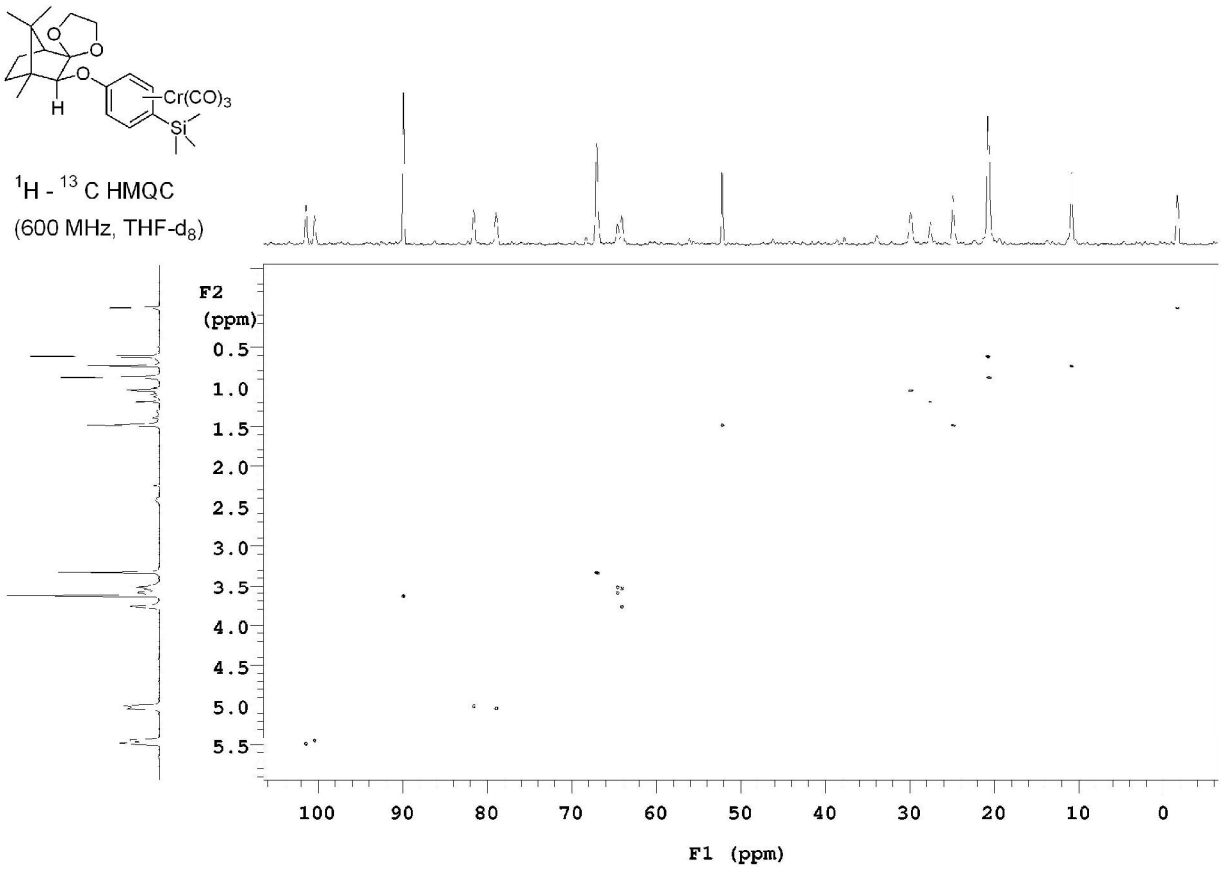


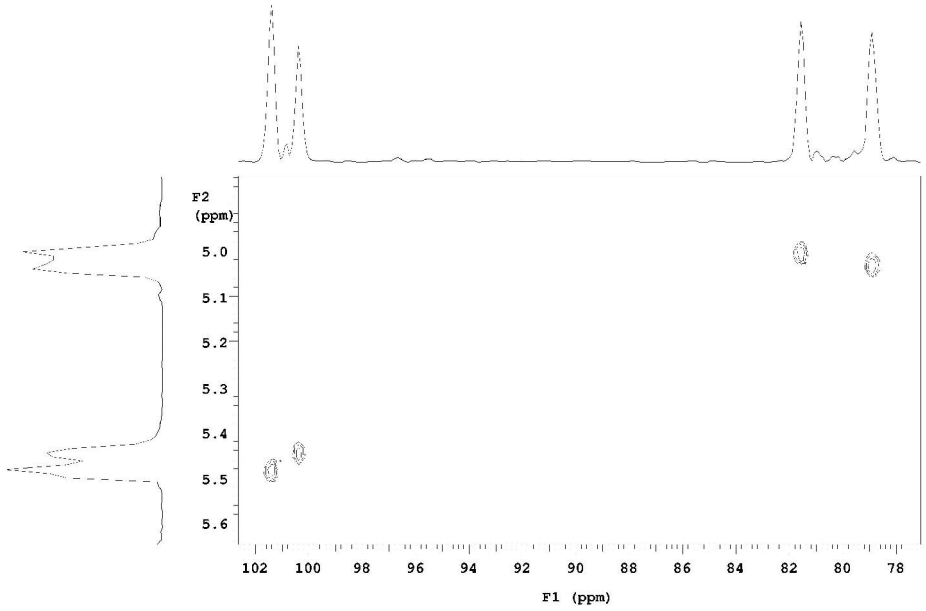
^{1}H-^{1}H COSY (600 MHz, THF-d_8) of **3c**



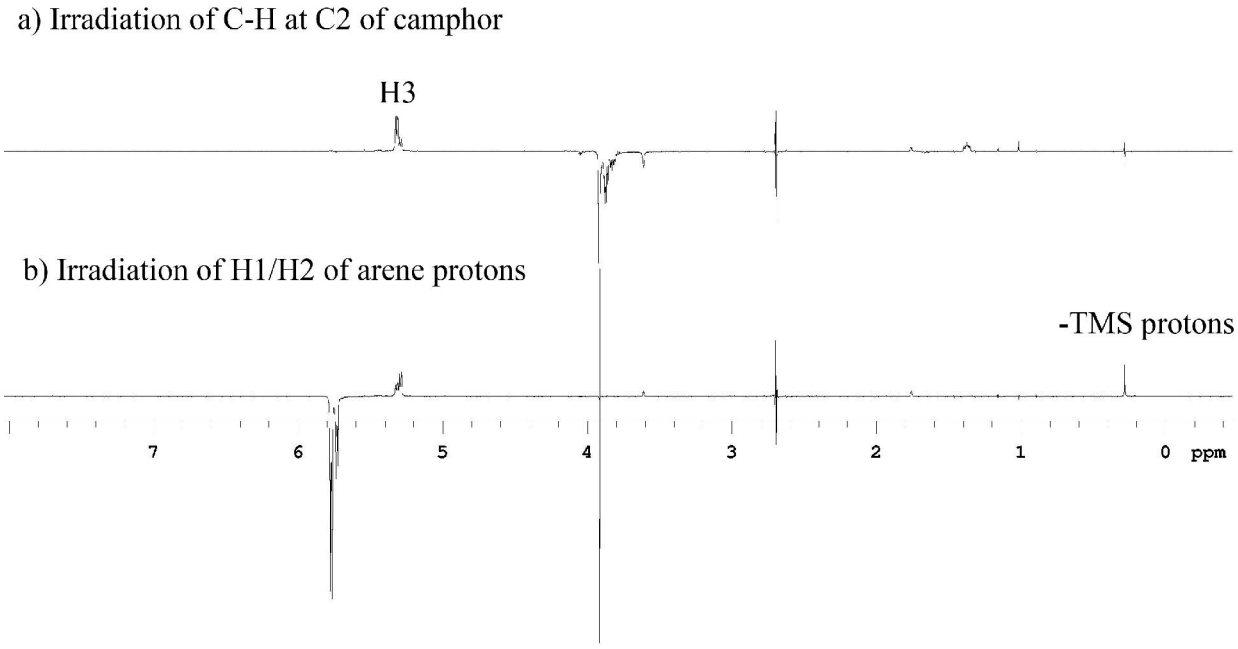


^{1}H-^{13}C HMQC (600 MHz, THF-d_8) of **3c**

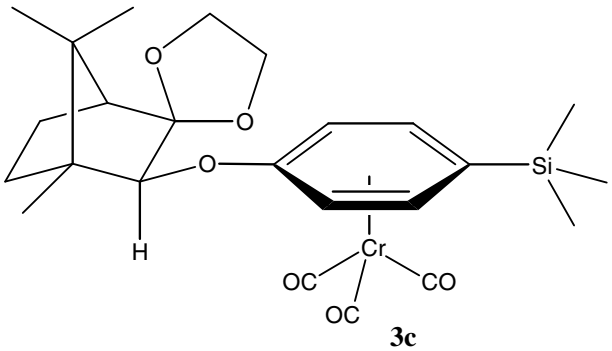




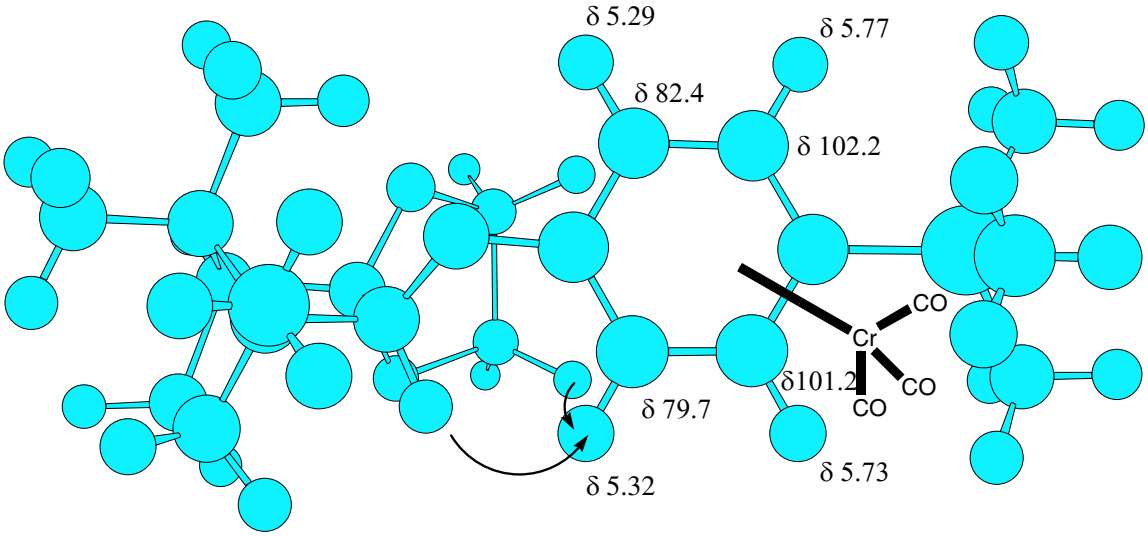
^{1}H NOE (600 MHz, THF-d_8) of **3c**

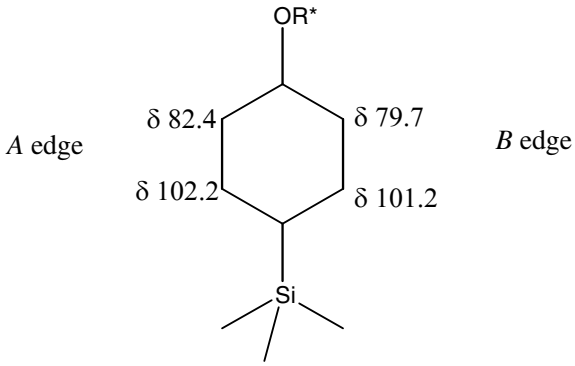


Representation of NOEs of complex **3c** (600 MHz, THF-d_8) and final assignment of arene carbons:

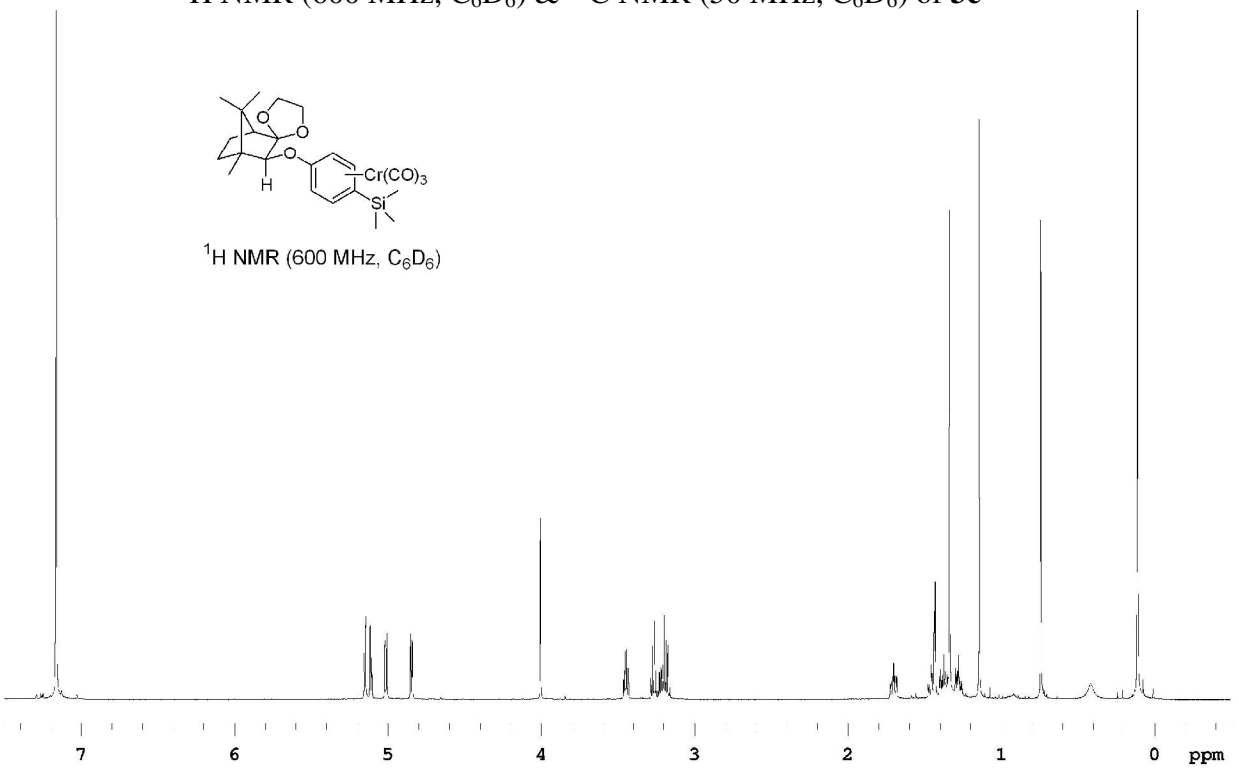


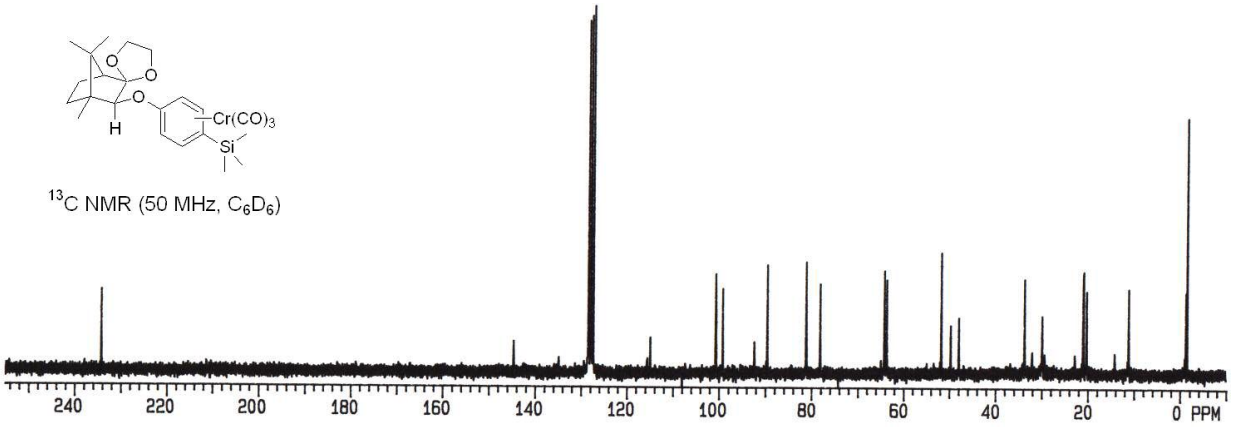
3c



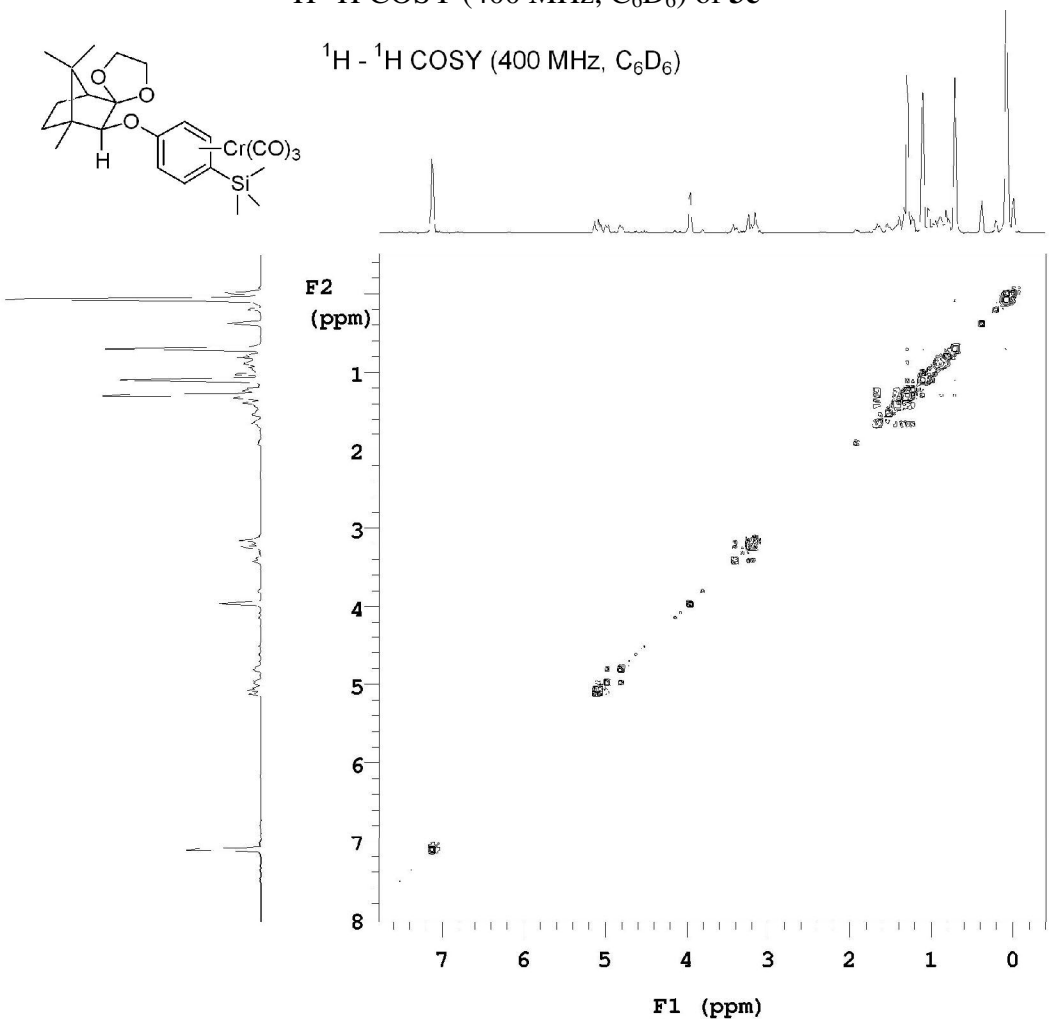


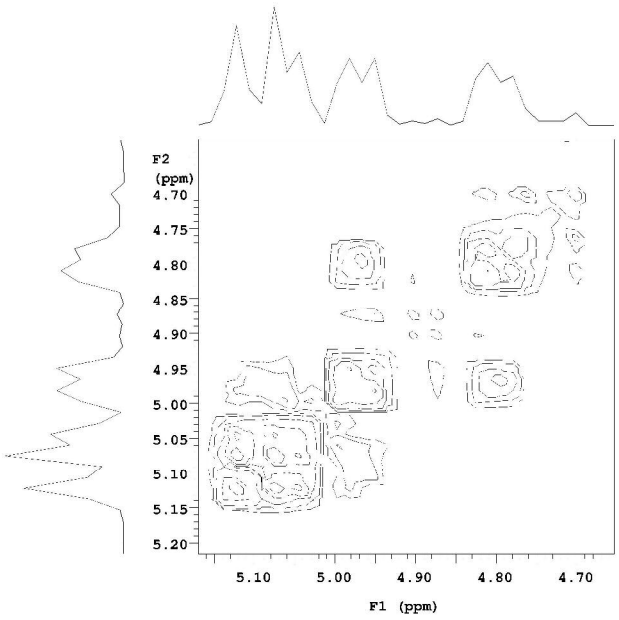
^{1}H NMR (600 MHz, C_6D_6) & ^{13}C NMR (50 MHz, C_6D_6) of **3c**



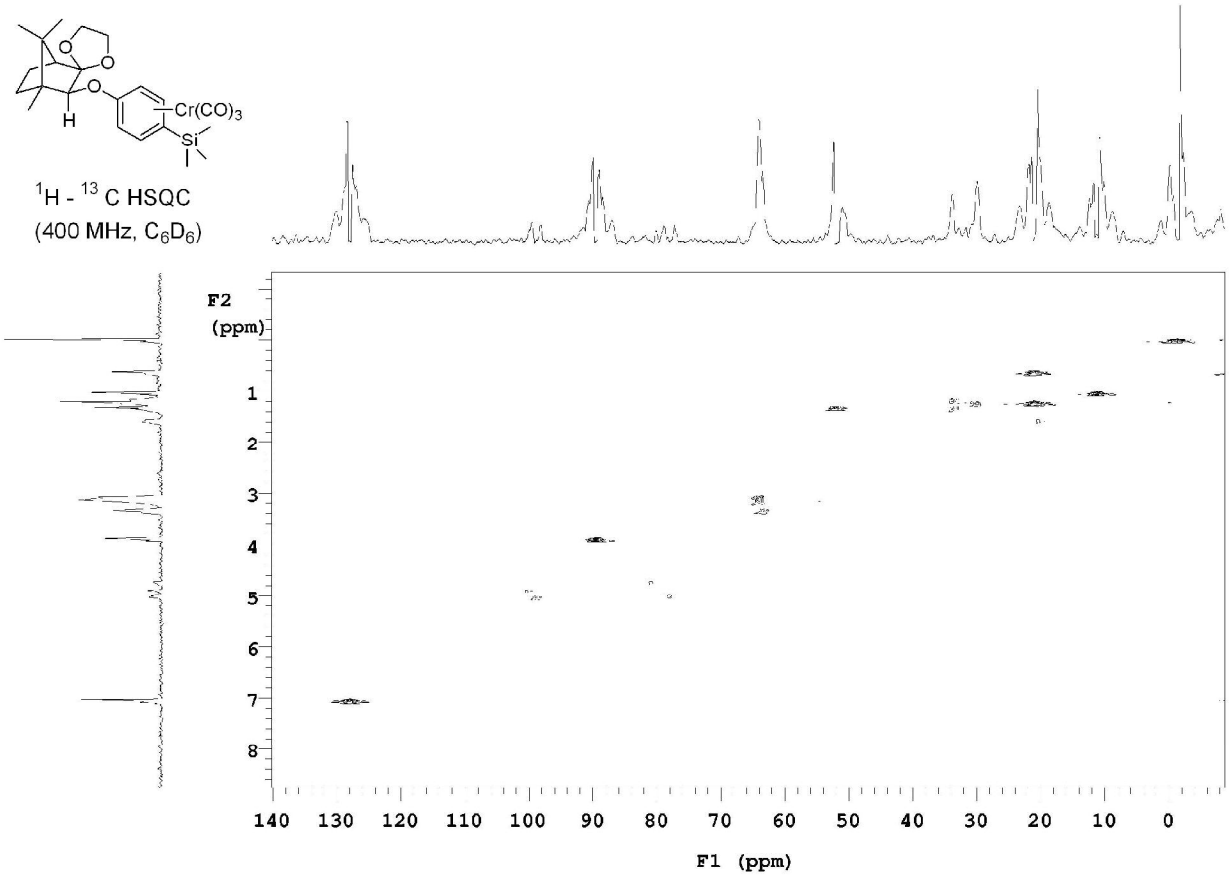


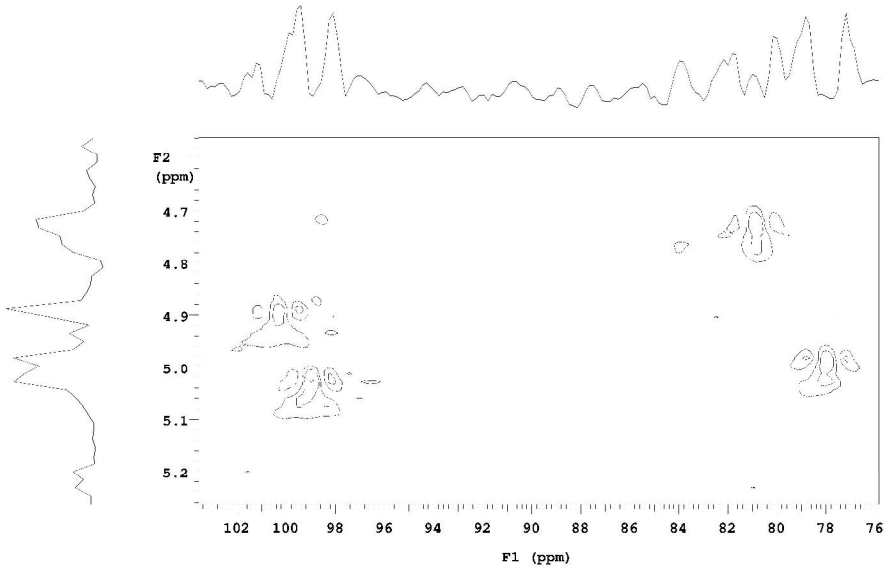
^{1}H-^{1}H COSY (400 MHz, C_6D_6) of **3c**





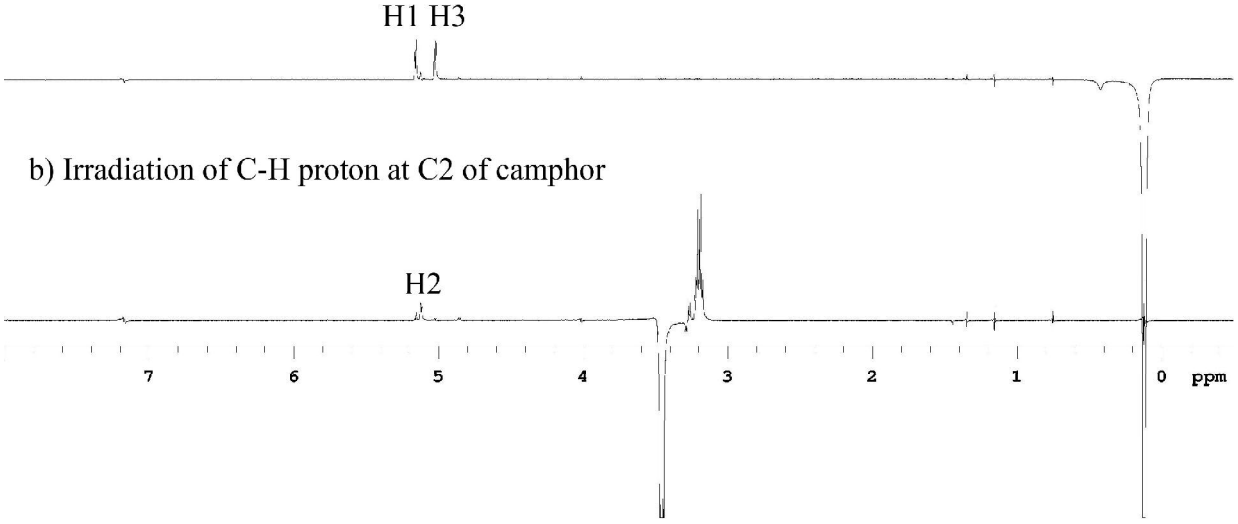
^{1}H-^{13}C HSQC (400 MHz, C_6D_6) of **3c**



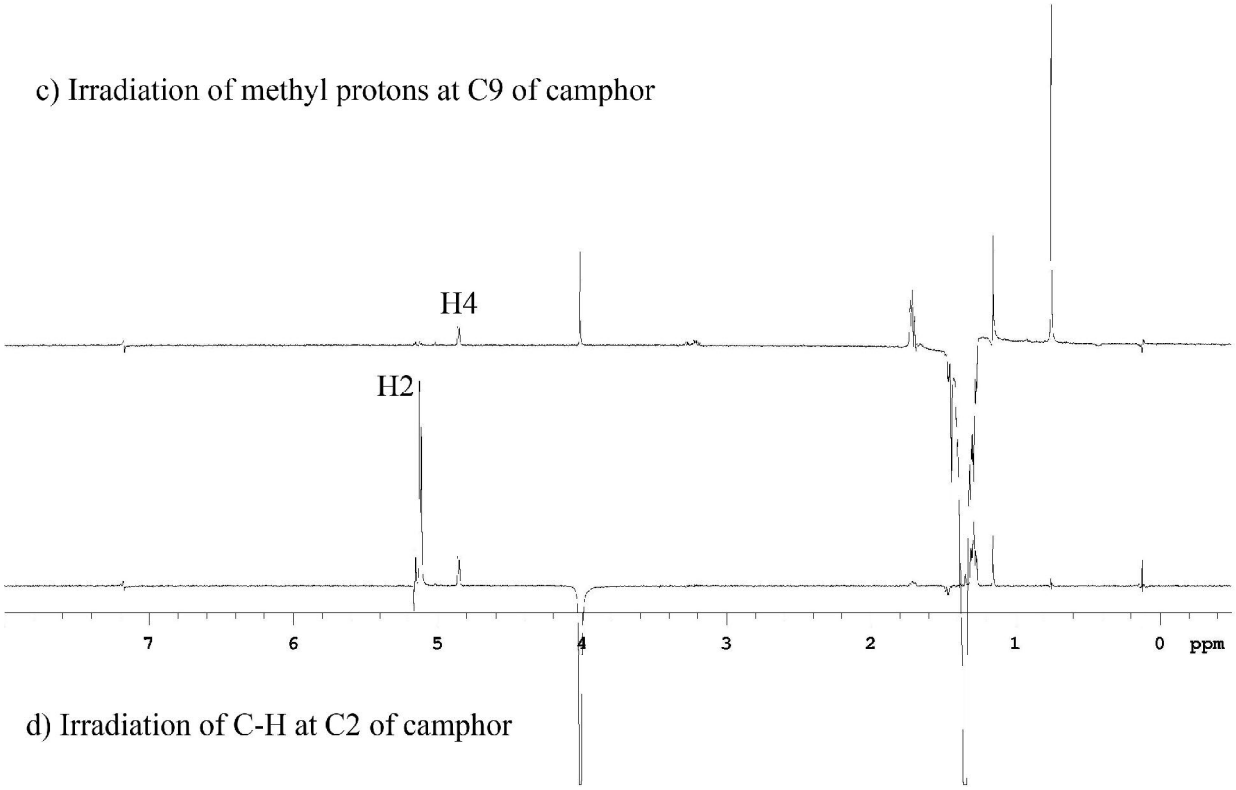


^{1}H NOE (600 MHz, C_6D_6) of **3c**

a) Irradiation of -TMS methyl protons

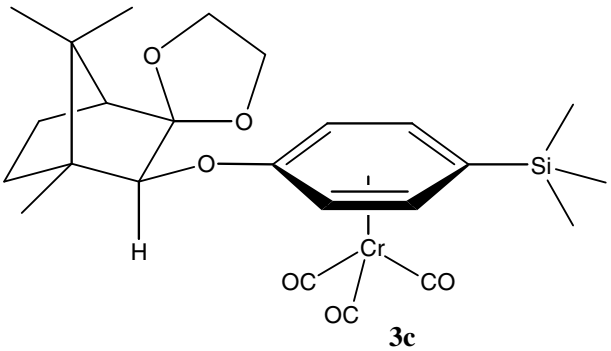


c) Irradiation of methyl protons at C9 of camphor

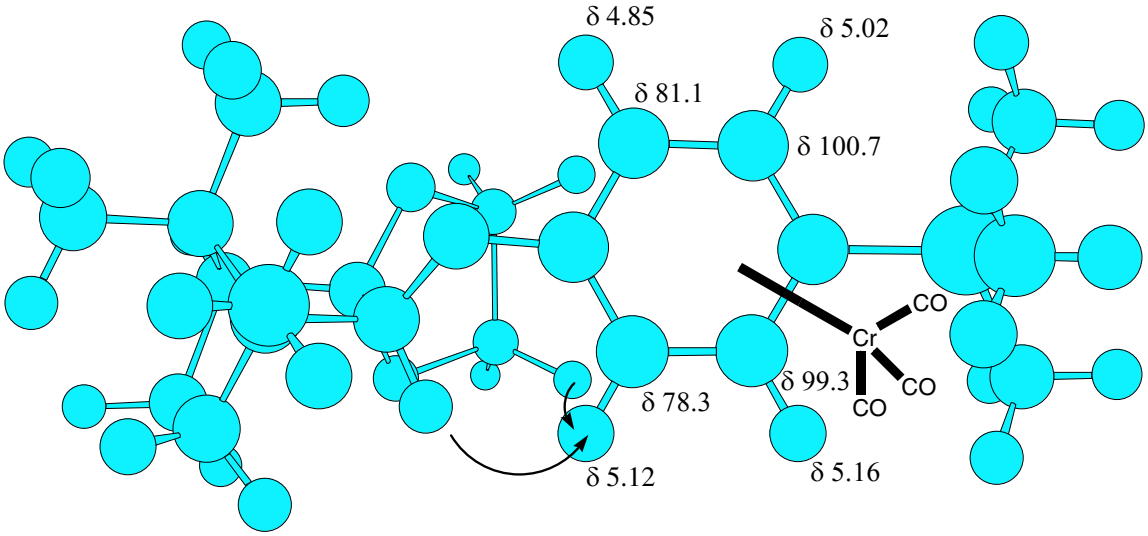


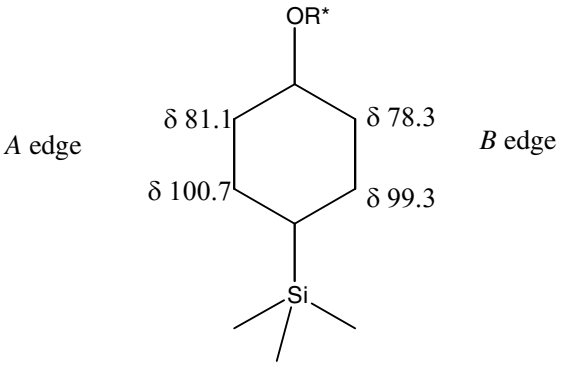
d) Irradiation of C-H at C2 of camphor

Representation of NOEs of complex **3c** (600 MHz,C_6D_6) and final assignment of arene carbons:



3c

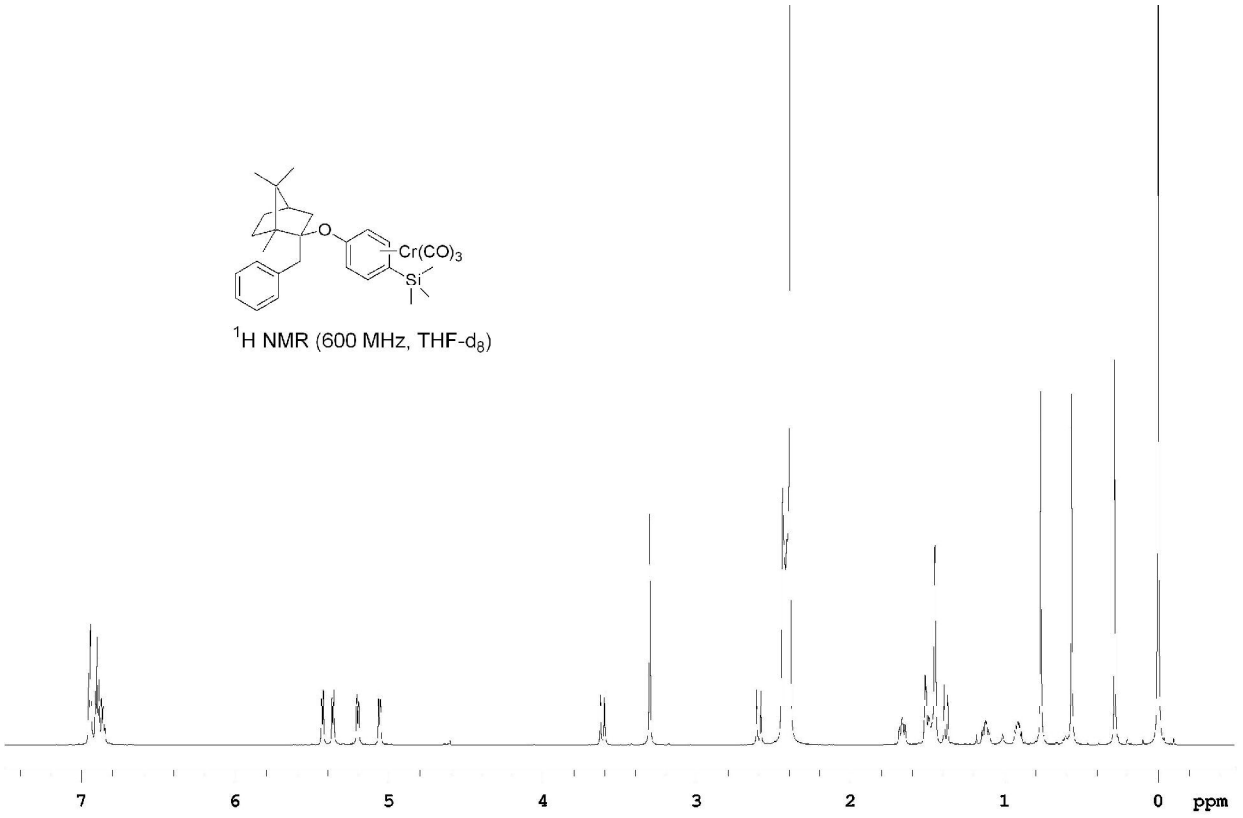


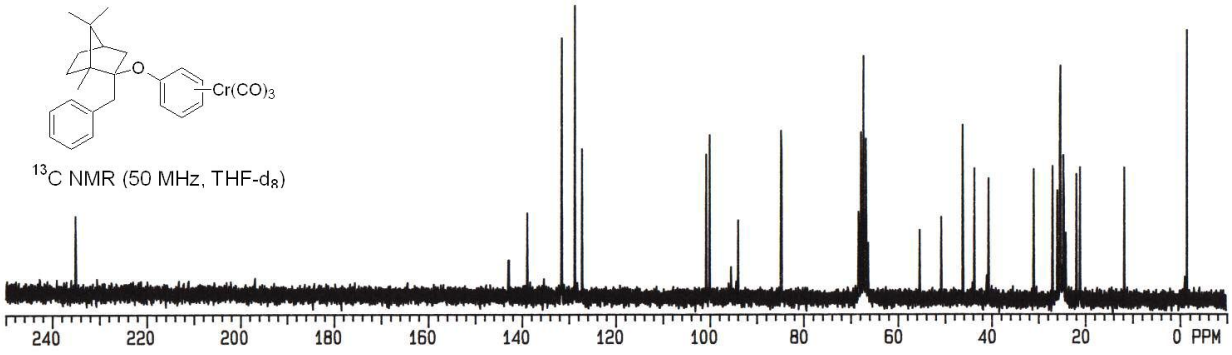


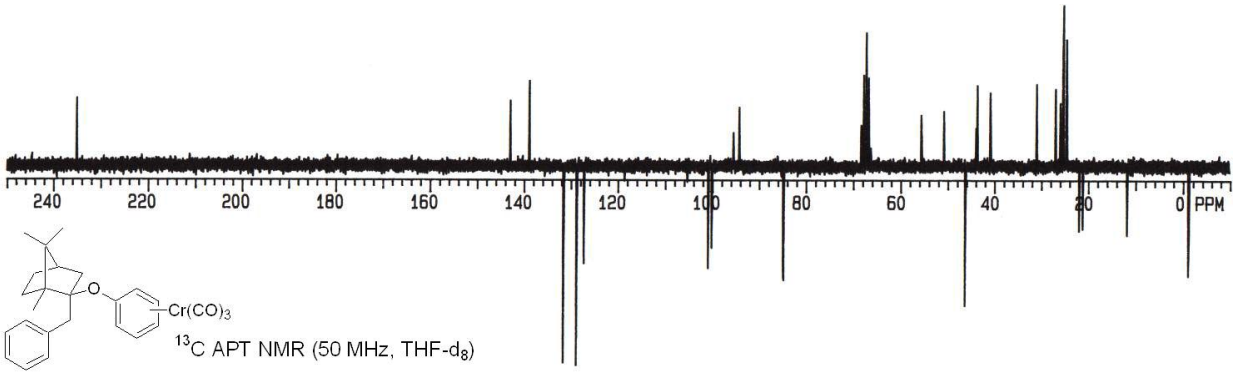
A edge

B edge

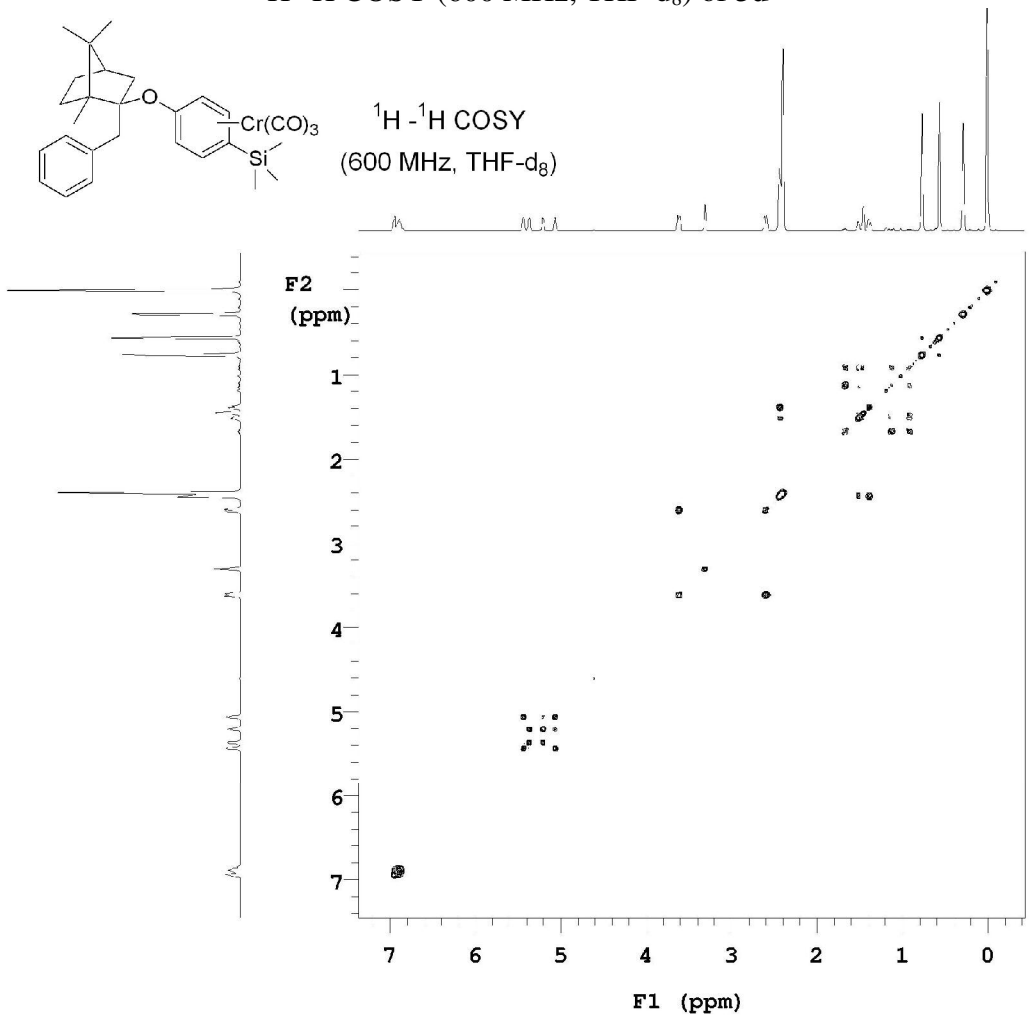
^{1}H NMR (600 MHz, THF-d_8) & ^{13}C NMR (50 MHz, THF-d_8) of **3d**

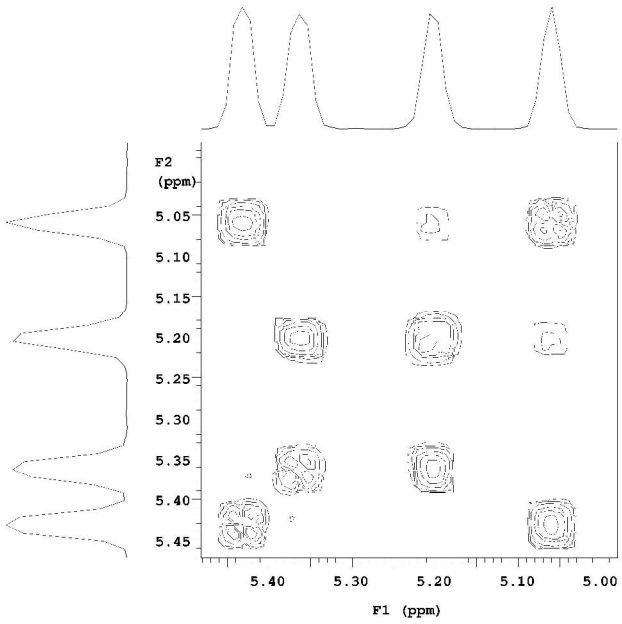




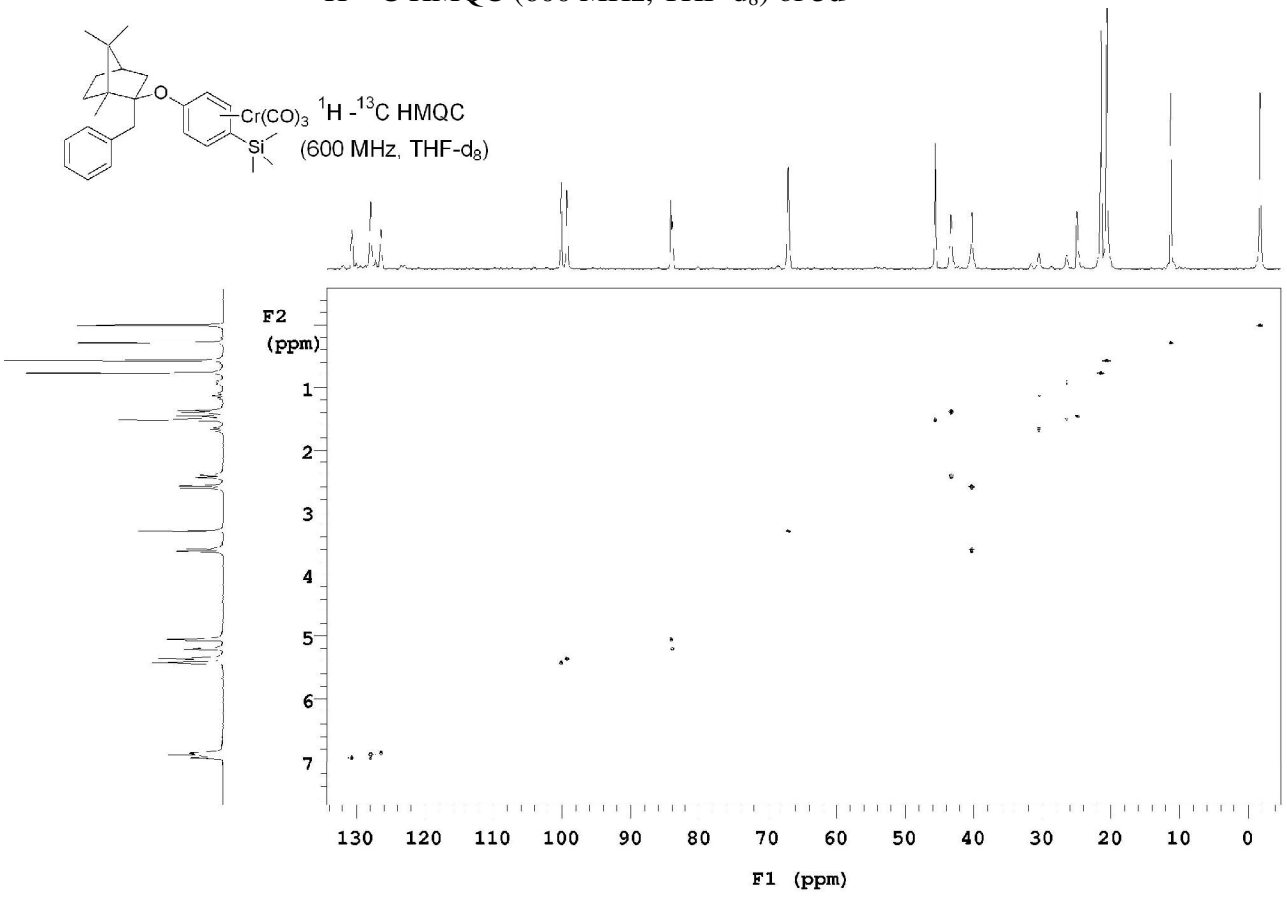


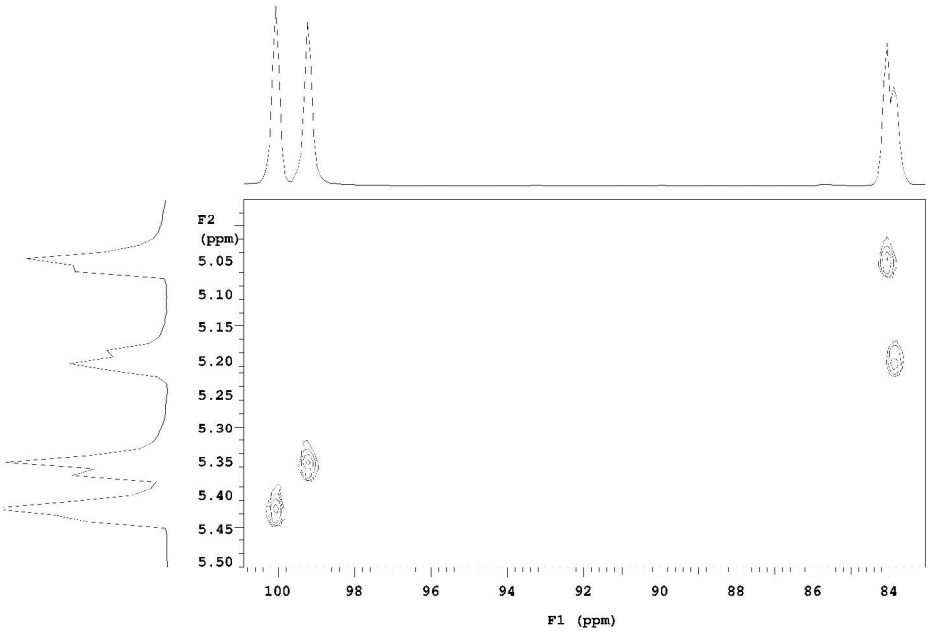
^{1}H-^{1}H COSY (600 MHz, THF-d_8) of **3d**





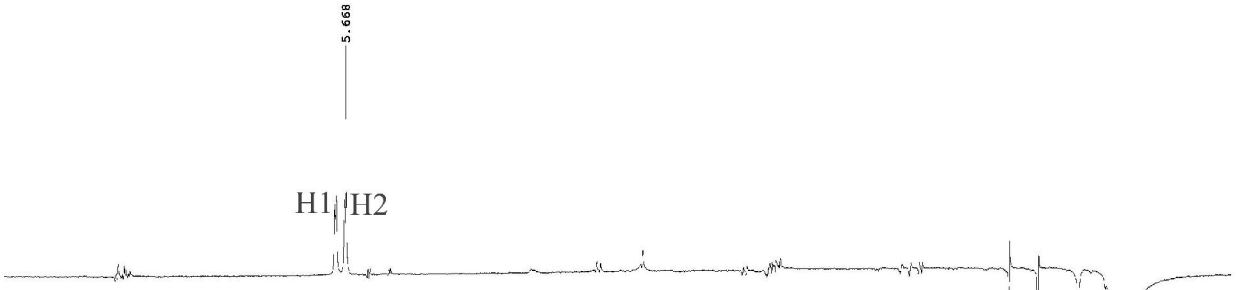
^{1}H-^{13}C HMQC (600 MHz, THF-d$_8$) of **3d**



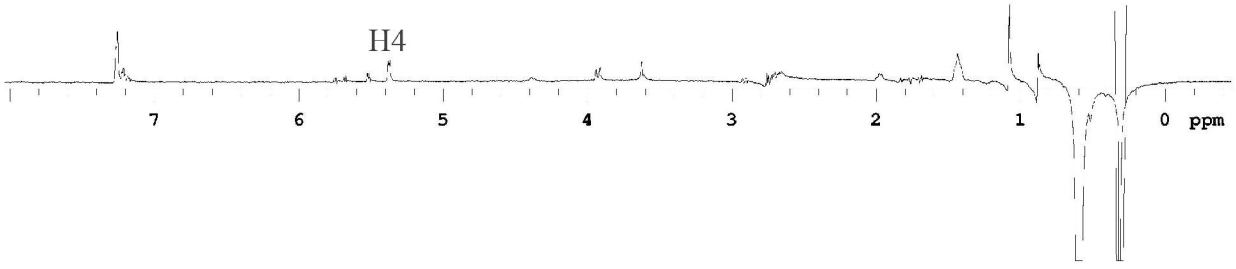


^{1}H NOE (600 MHz, THF-d_8) of **3d**

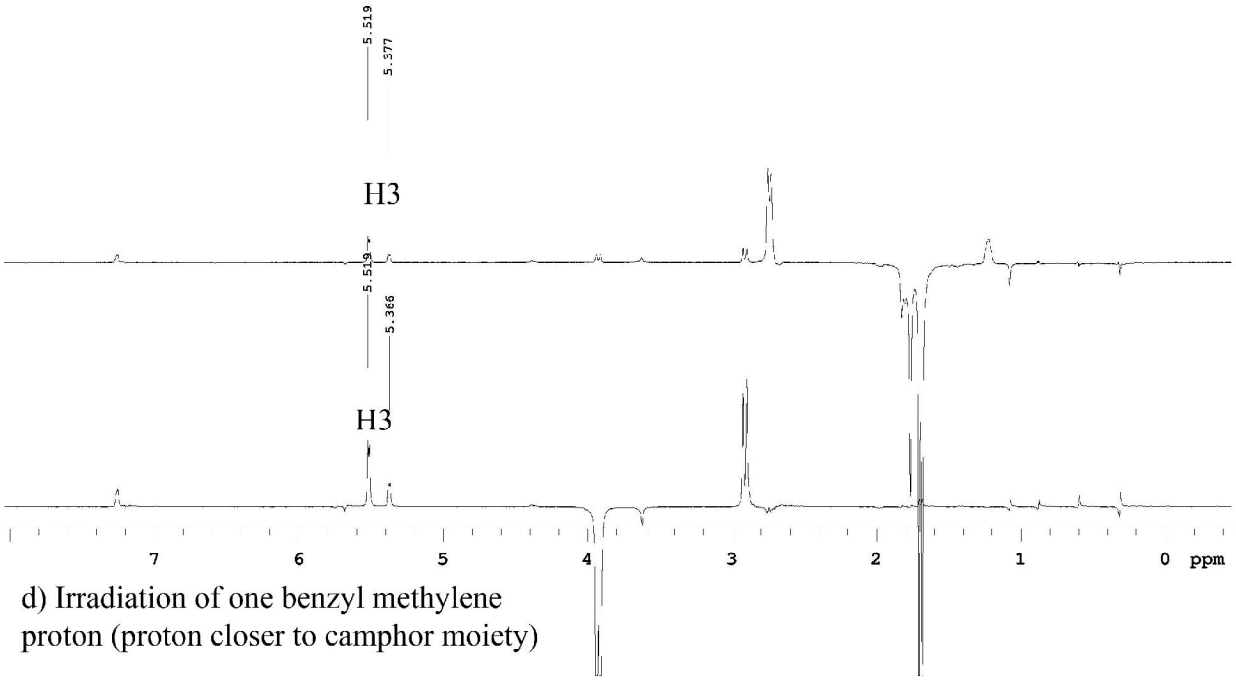
a) Irradiation of -TMS methyl protons



b) Irradiation of C10 Methyl of camphor

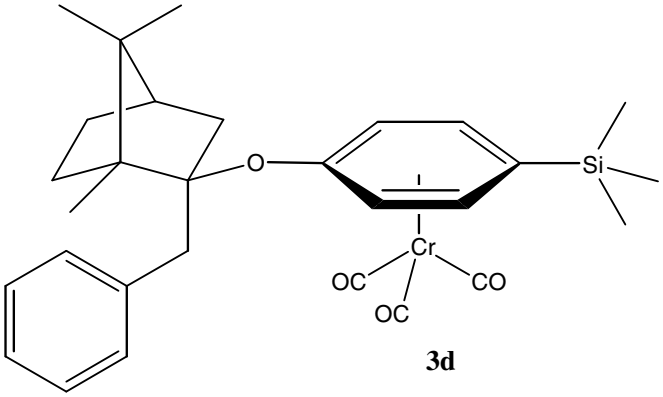


c) Irradiation of *endo* proton at C3 of camphor

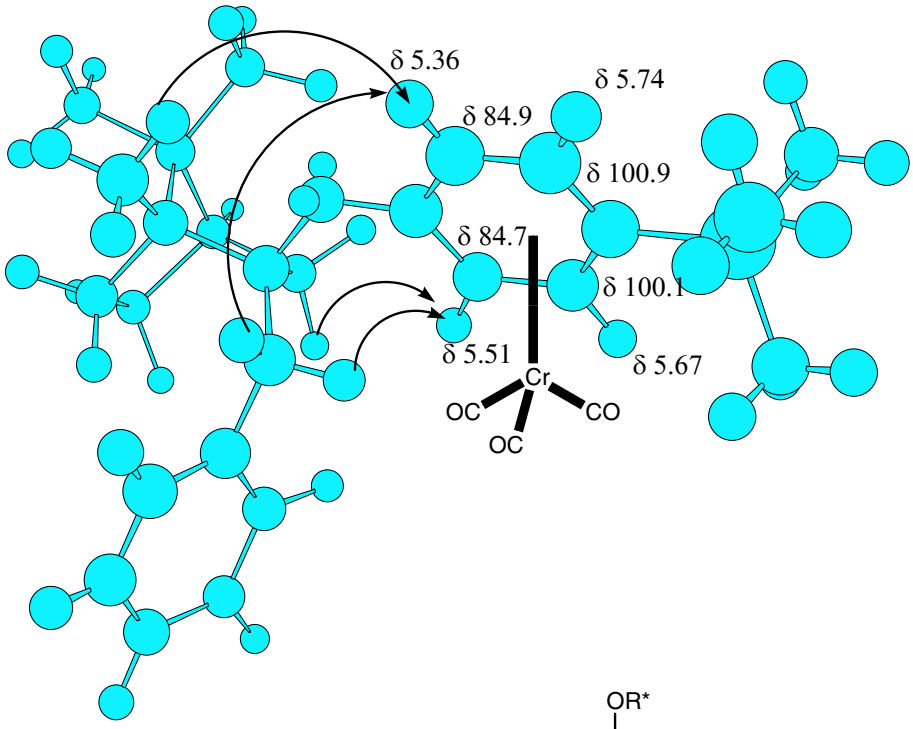


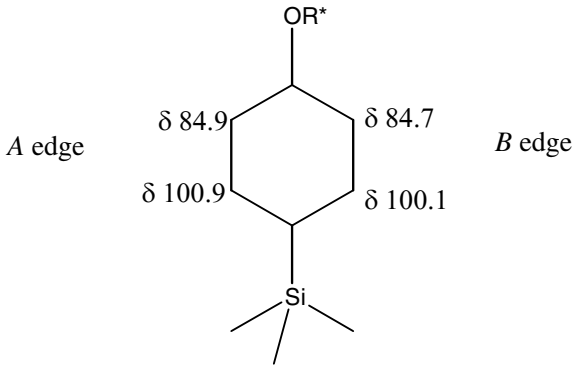
d) Irradiation of one benzyl methylene proton (proton closer to camphor moiety)

Representation of NOEs of complex **3d** (600 MHz, THF-d_8) and final assignment of arene carbons:



3d

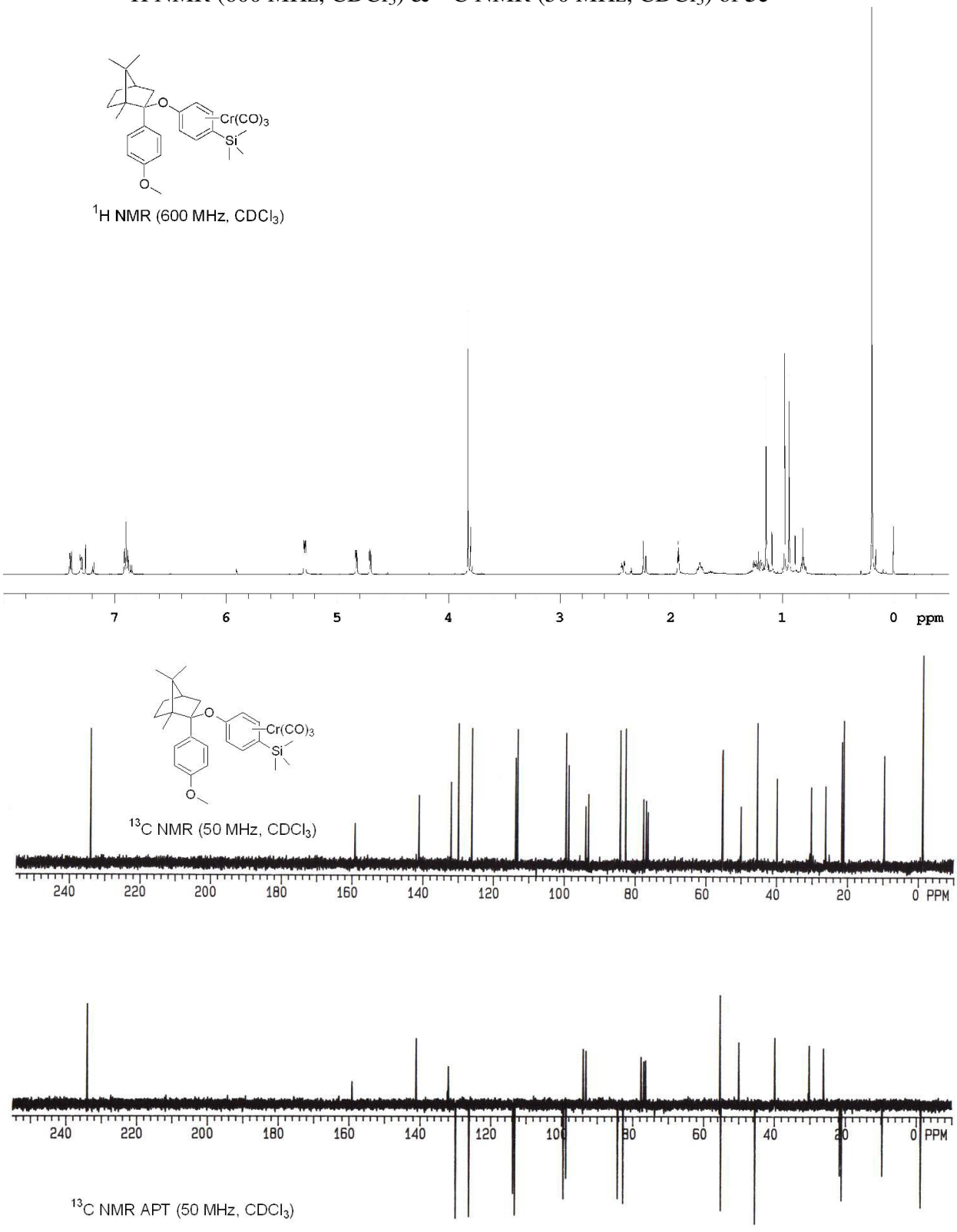




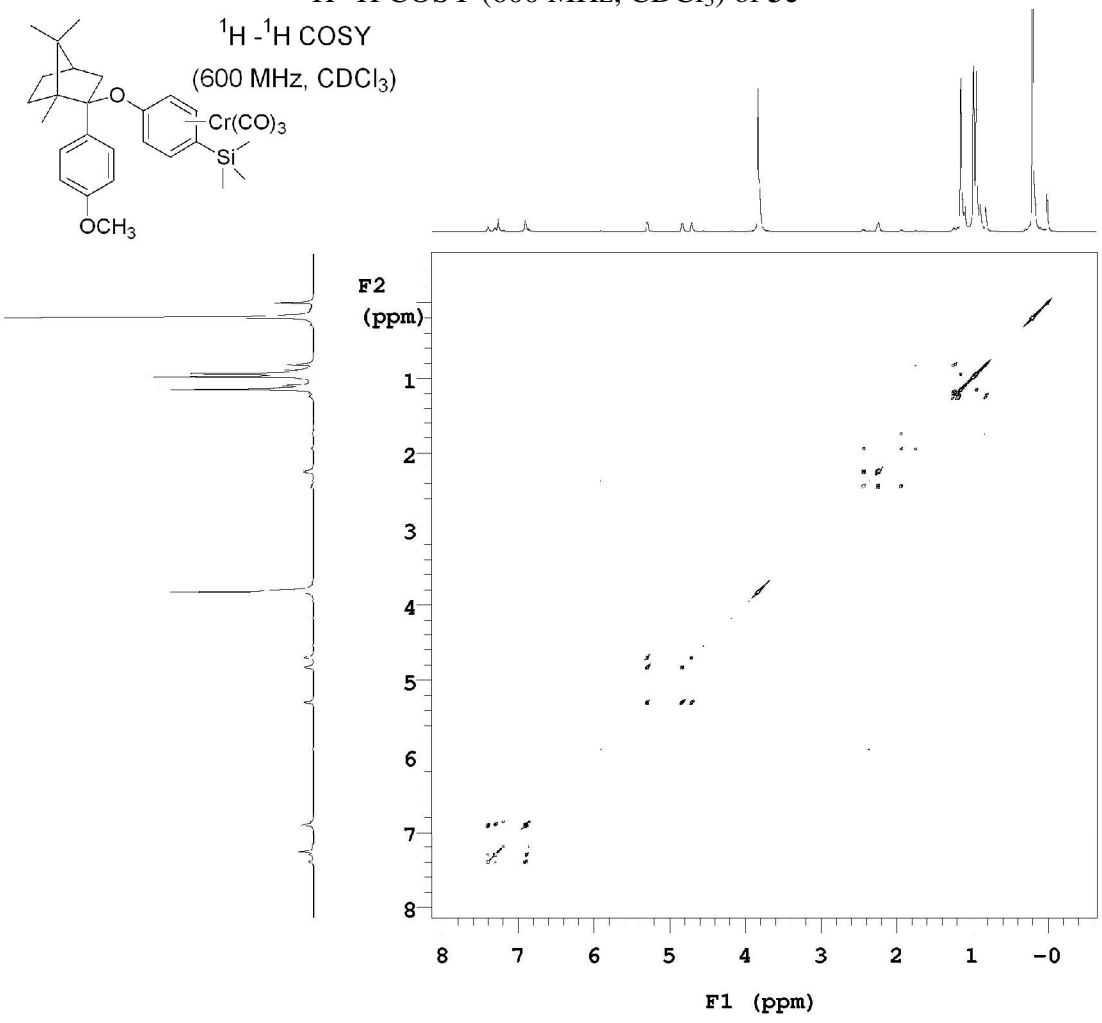
A edge

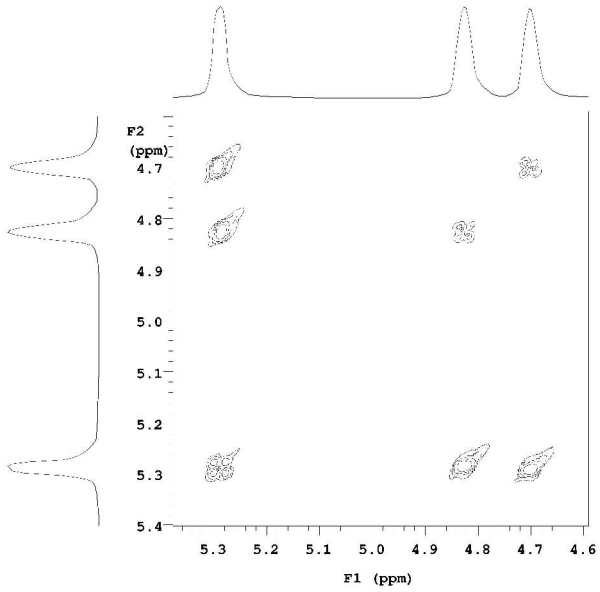
B edge

^{1}H NMR (600 MHz, $CDCl_3$) & ^{13}C NMR (50 MHz, $CDCl_3$) of **3e**

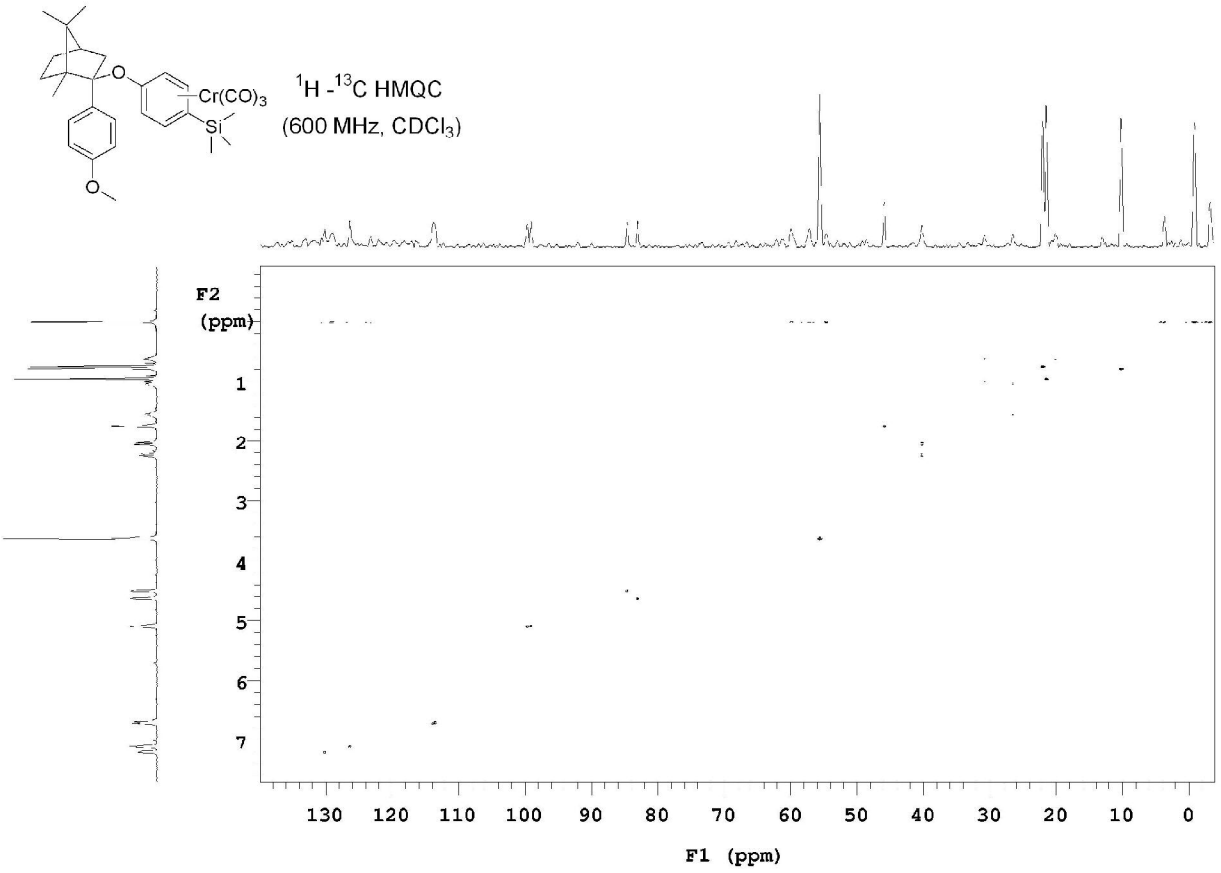


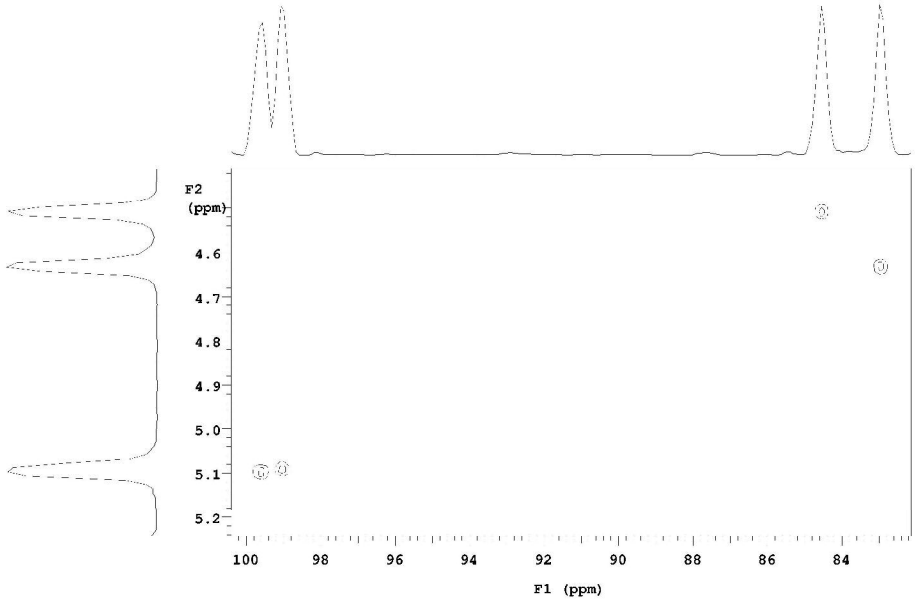
^{1}H-^{1}H COSY (600 MHz, $CDCl_3$) of **3e**



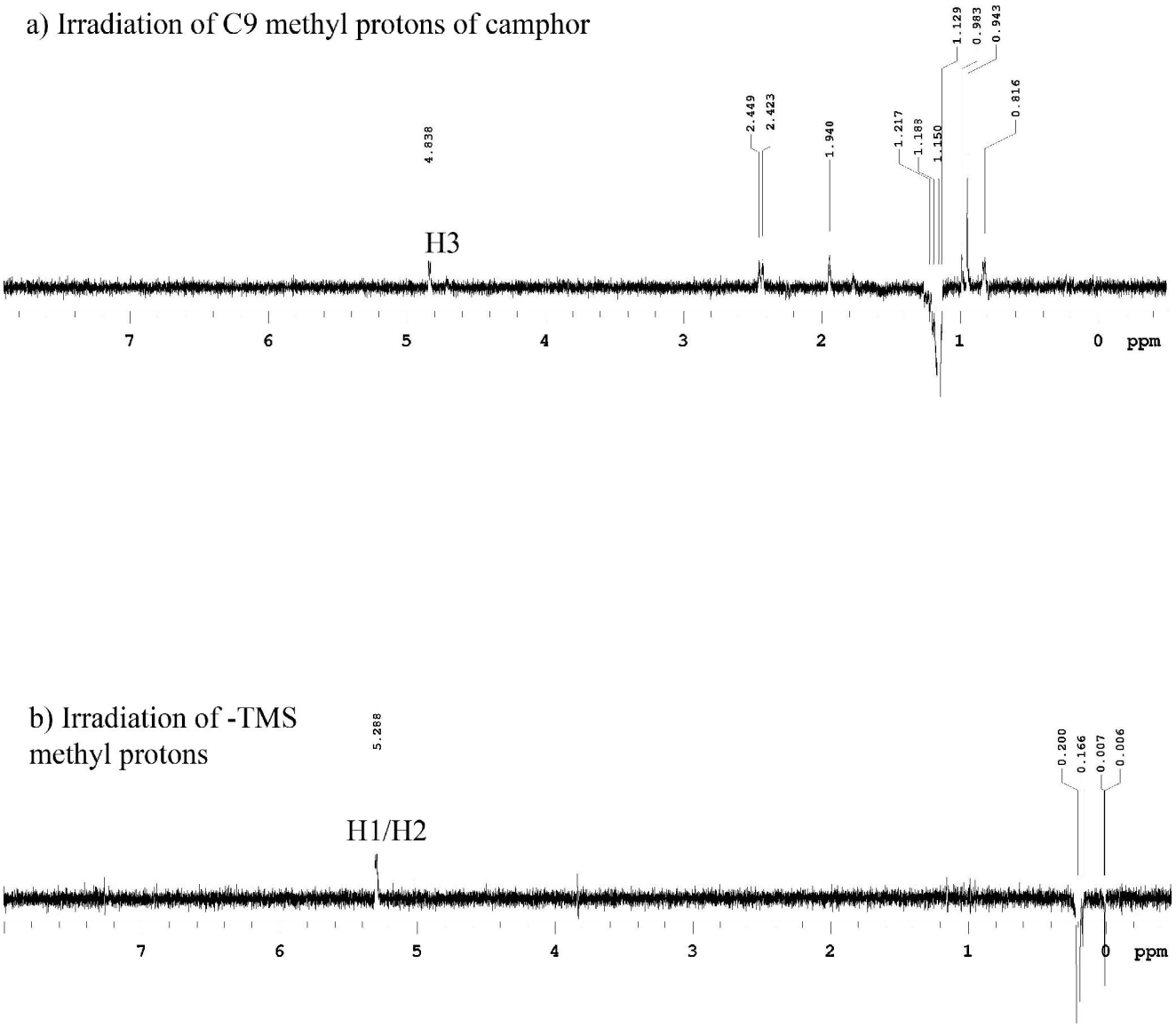


^{1}H-^{13}C HMQC (600 MHz, $CDCl_3$) of **3e**

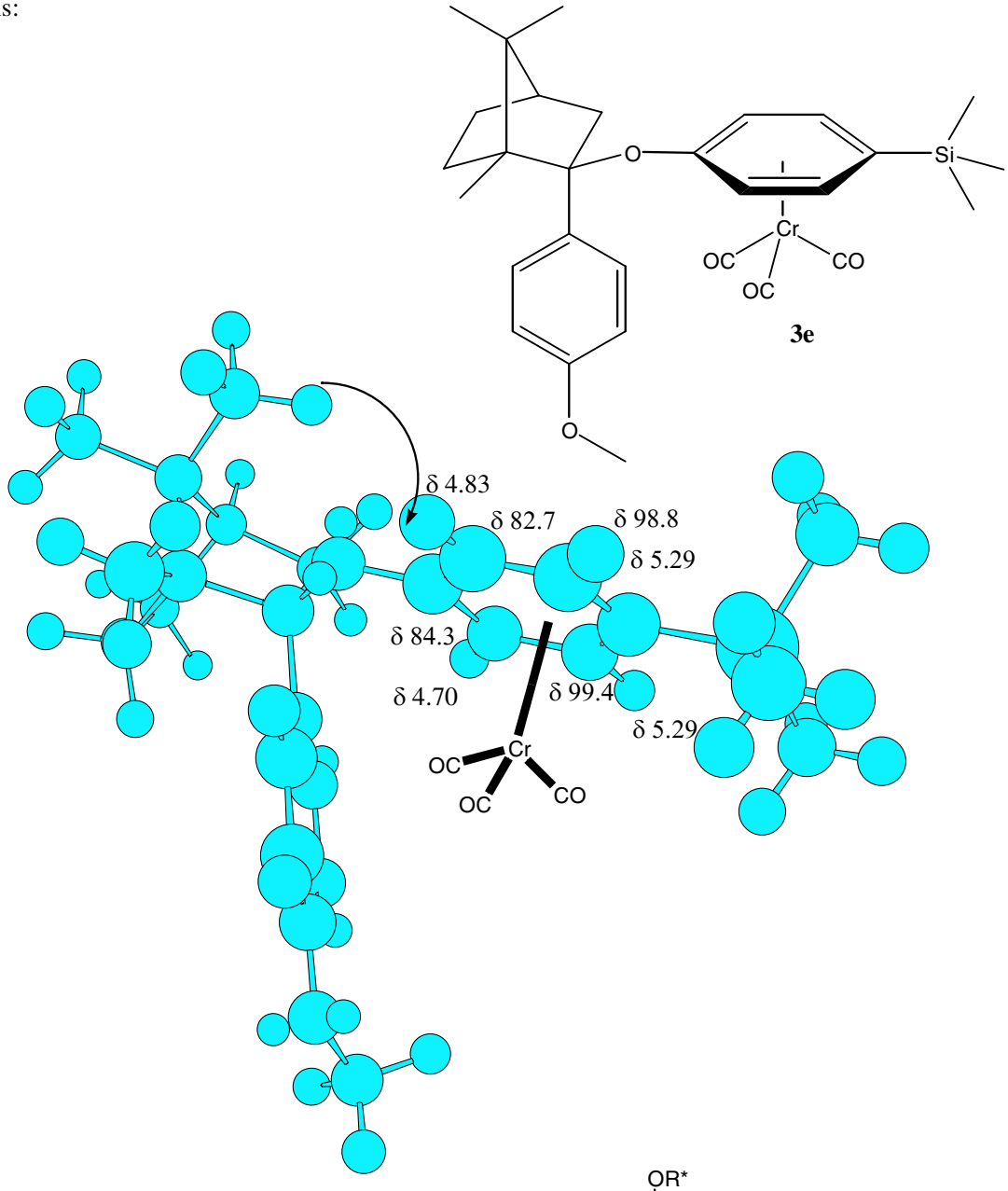




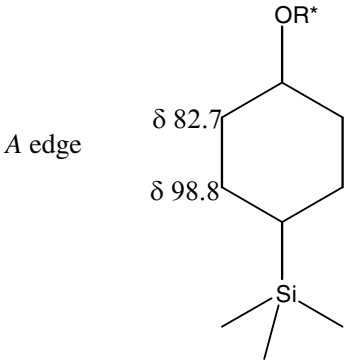
^{1}H NOE (600 MHz, $CDCl_3$) of **3e**



Representation of NOEs of complex **3e** NOE (600 MHz, $CDCl_3$)and final assignment of arene carbons:



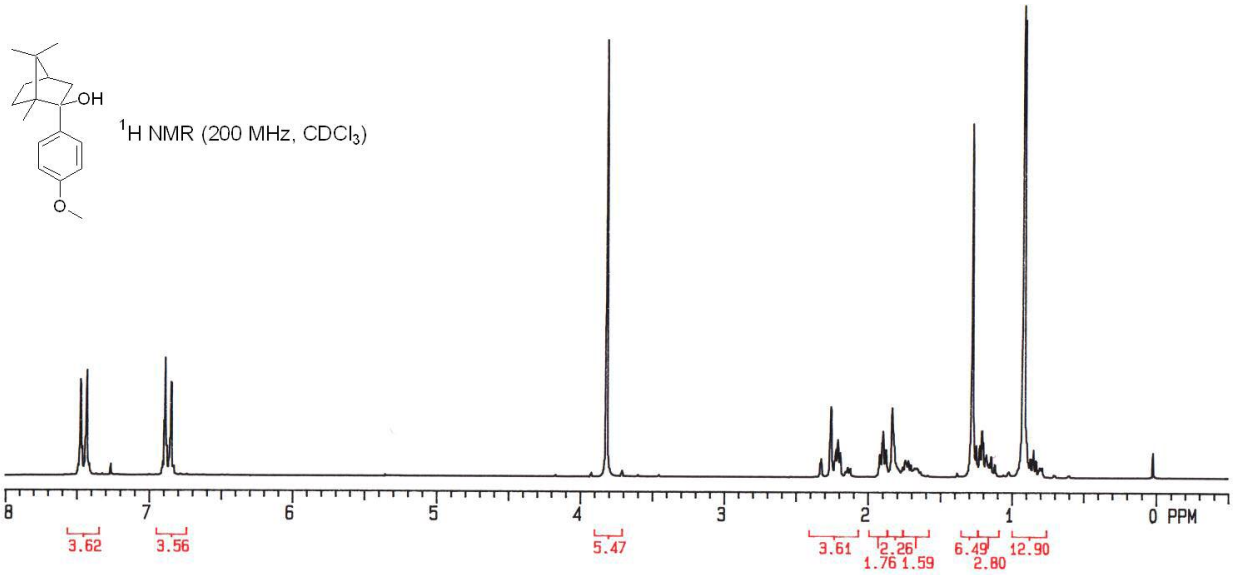
3e

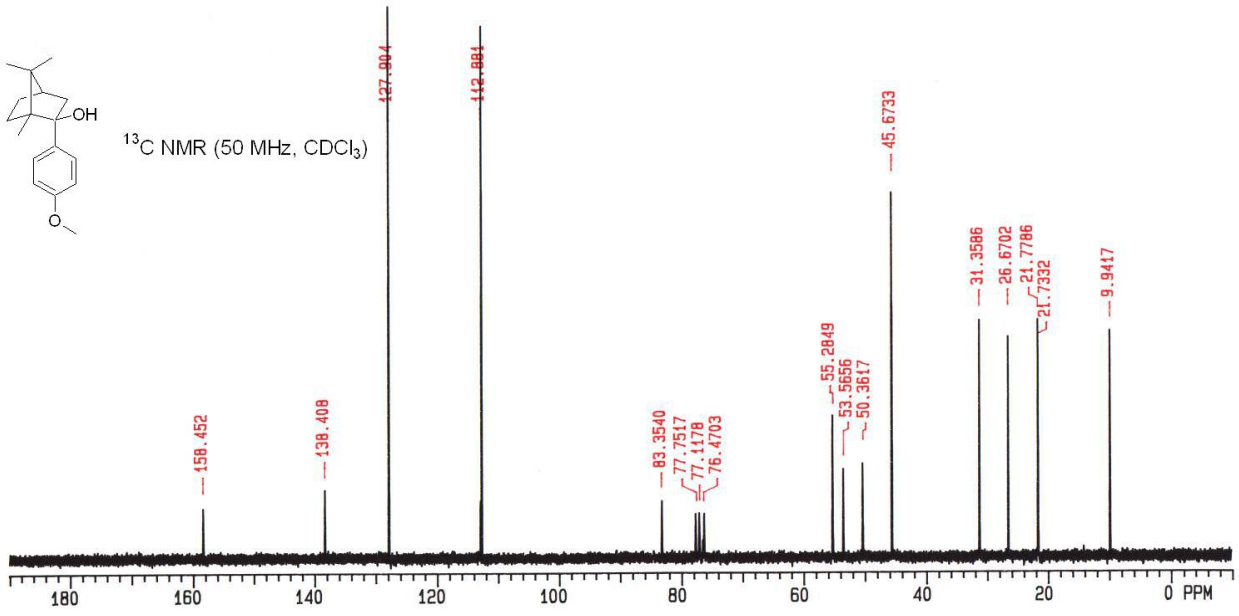


A edge

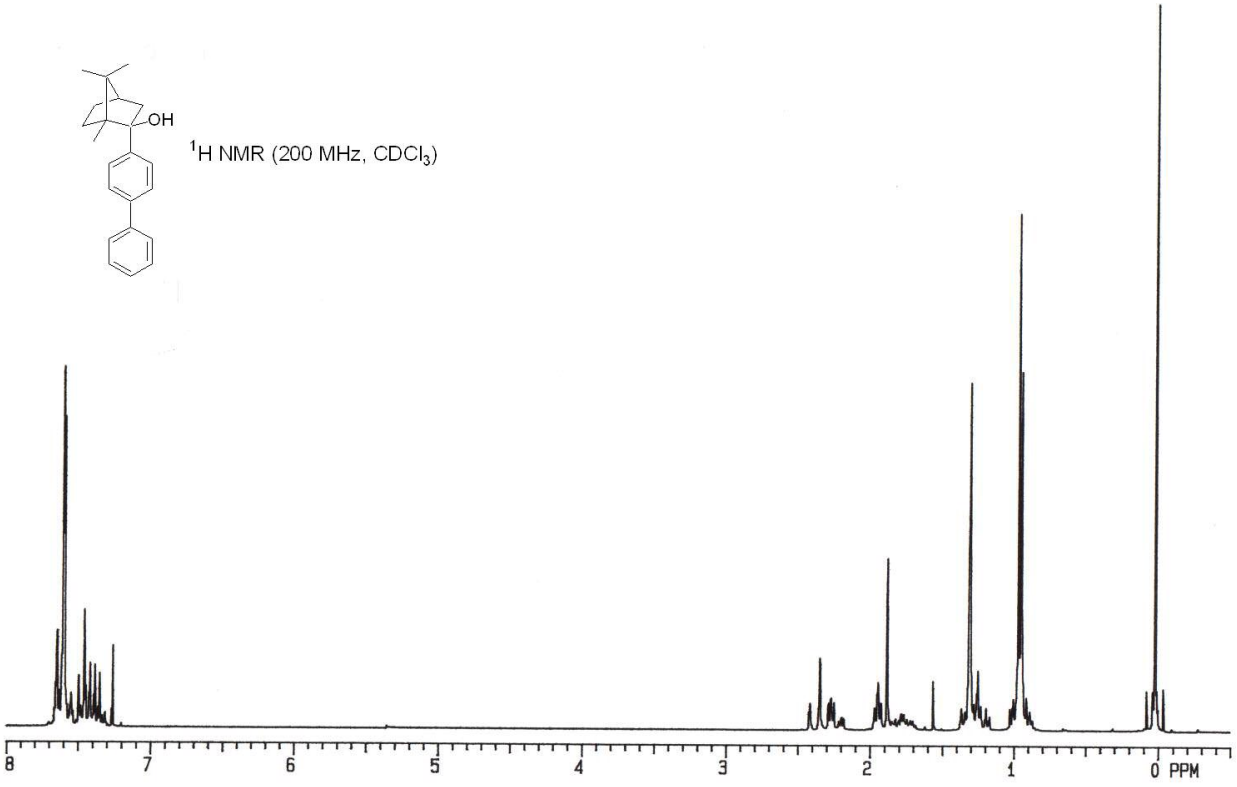
B edge

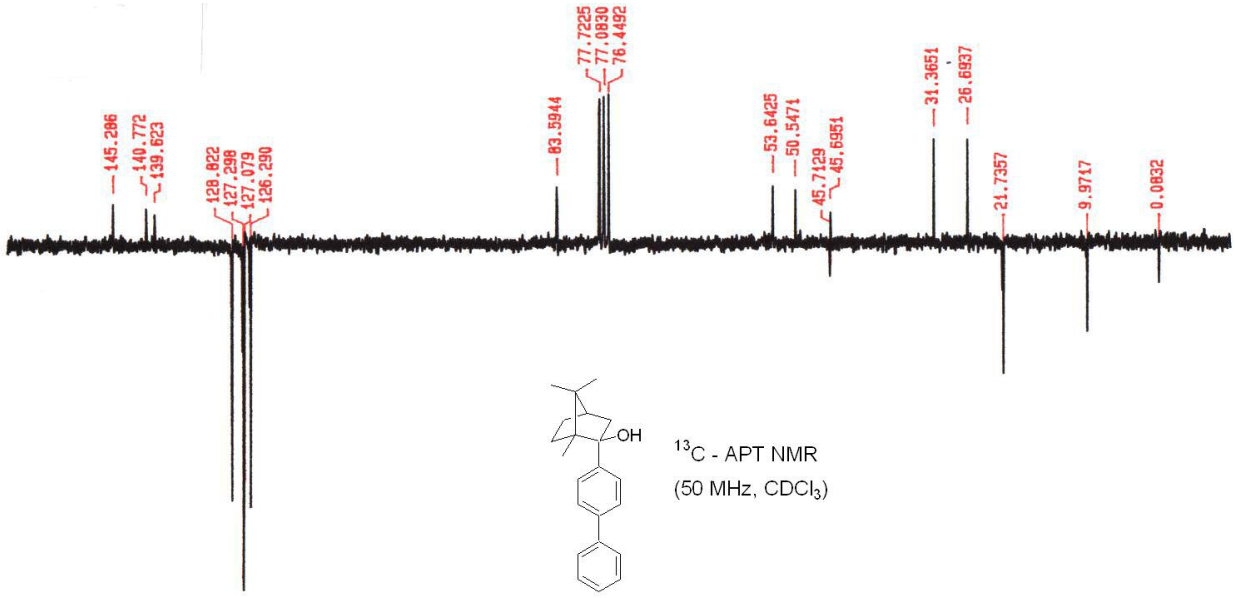
^{1}H NMR (200 MHz, $CDCl_3$) and ^{13}C NMR (50 MHz, $CDCl_3$) of **2e**





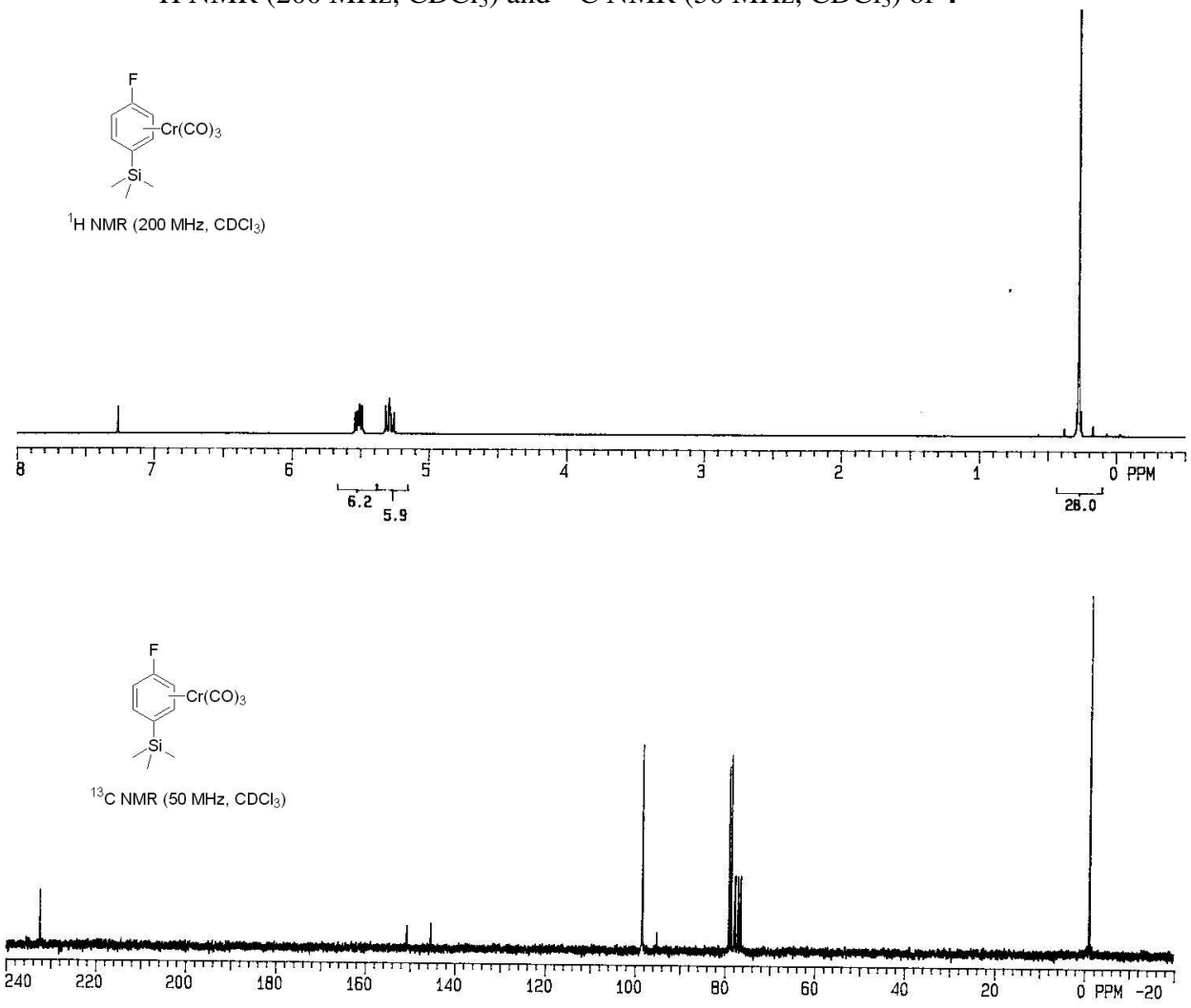
^{1}H NMR (200 MHz, $CDCl_3$) and ^{13}C APT NMR (50 MHz, $CDCl_3$) of **2f**

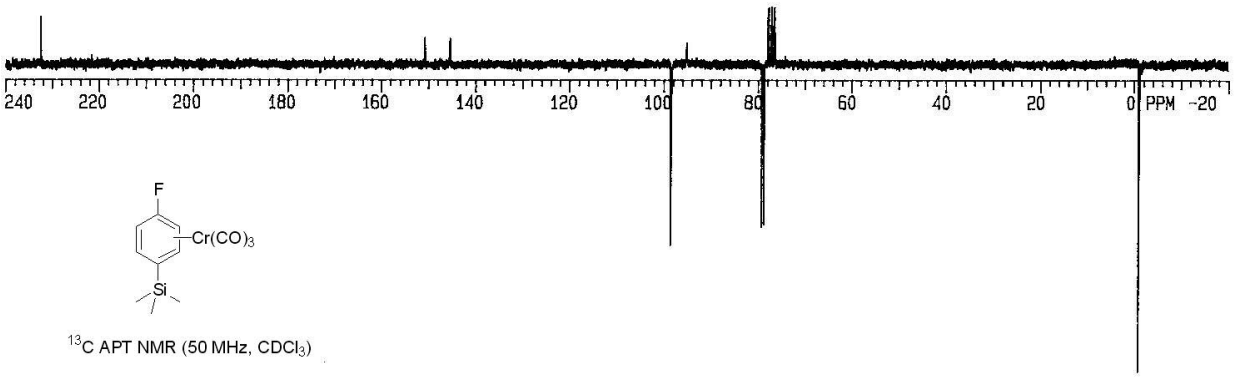




^{13}C - APT NMR
(50 MHz, $CDCl_3$)

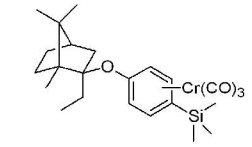
^{1}H NMR (200 MHz, $CDCl_3$) and ^{13}C NMR (50 MHz, $CDCl_3$) of **4**



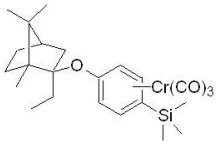


^{13}C APT NMR (50 MHz, $CDCl_3$)

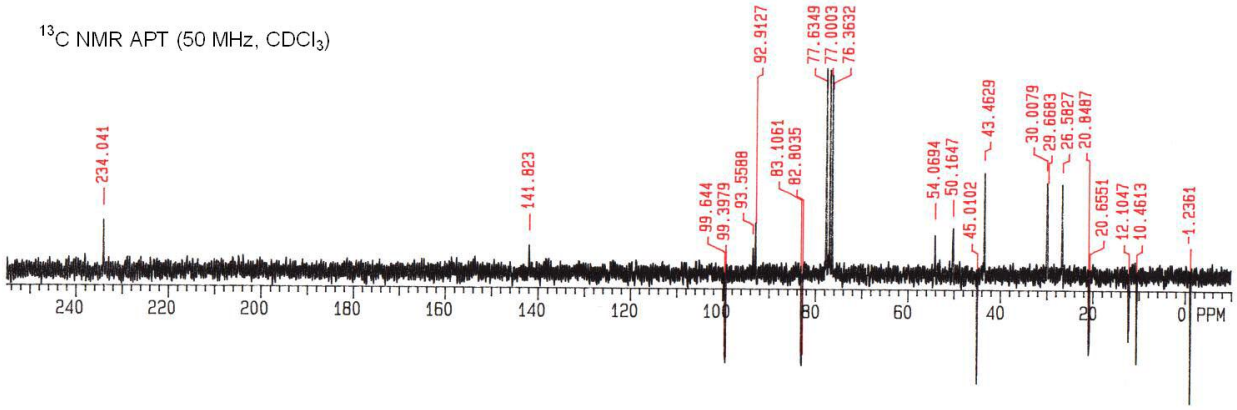
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (50 MHz, $CDCl_3$) of **3g**



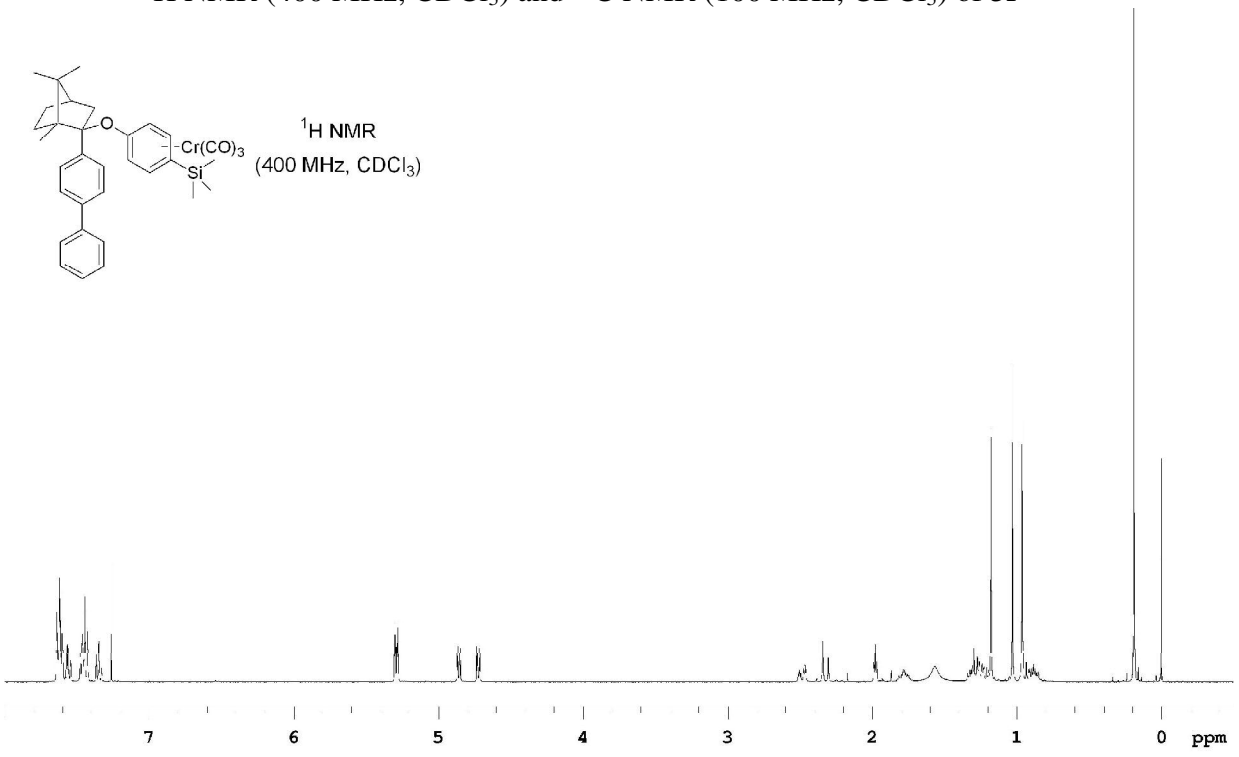
^{1}H NMR (400 MHz, $CDCl_3$)

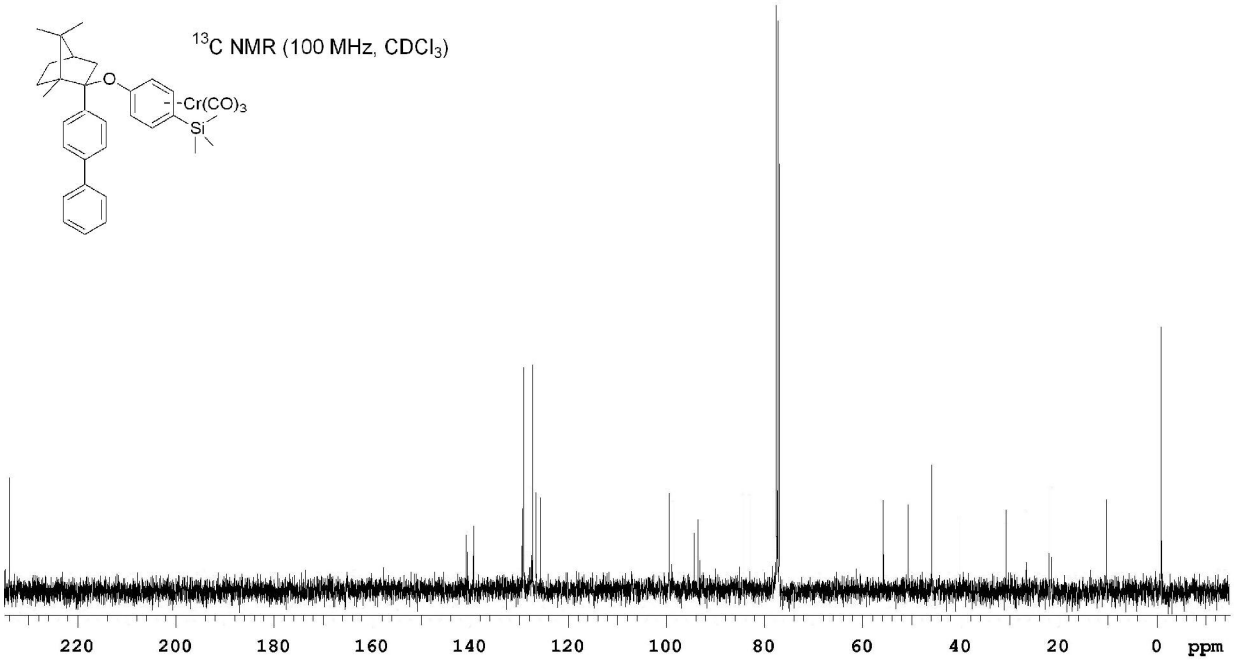


^{13}C NMR (50 MHz, $CDCl_3$)

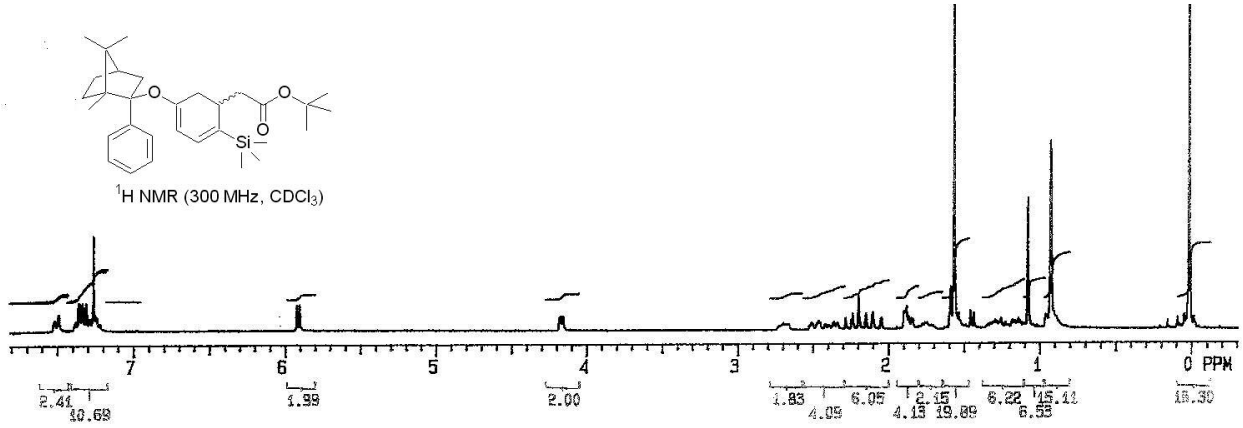


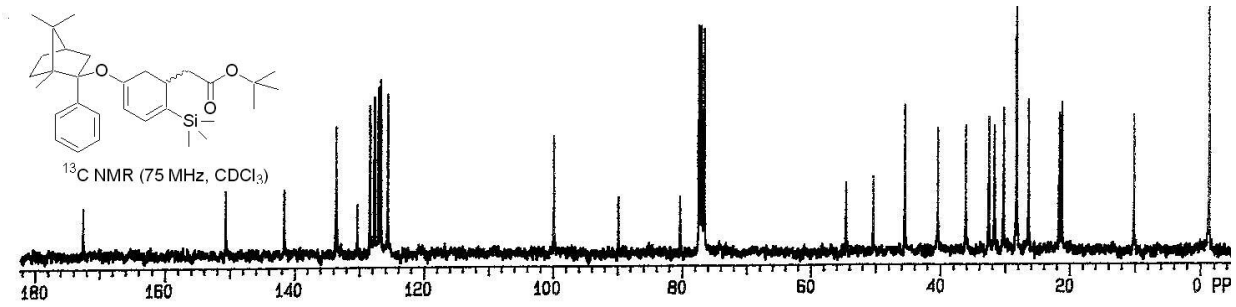
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **3f**



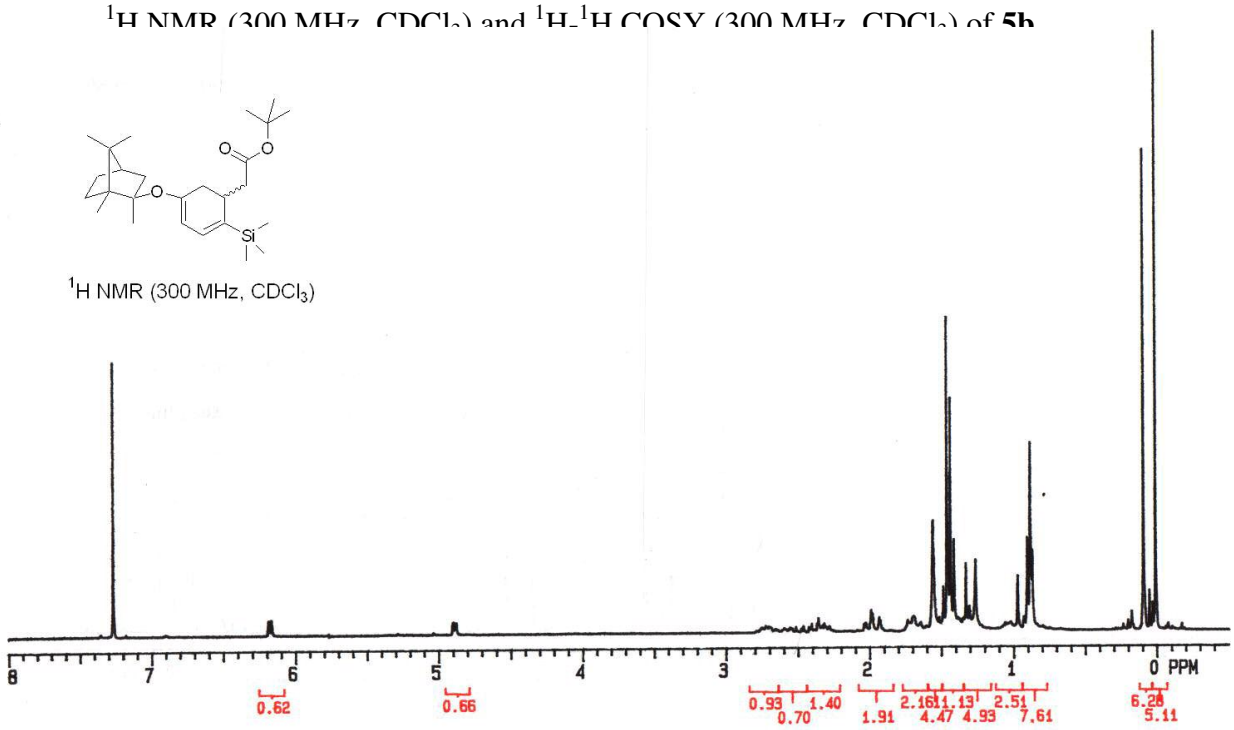


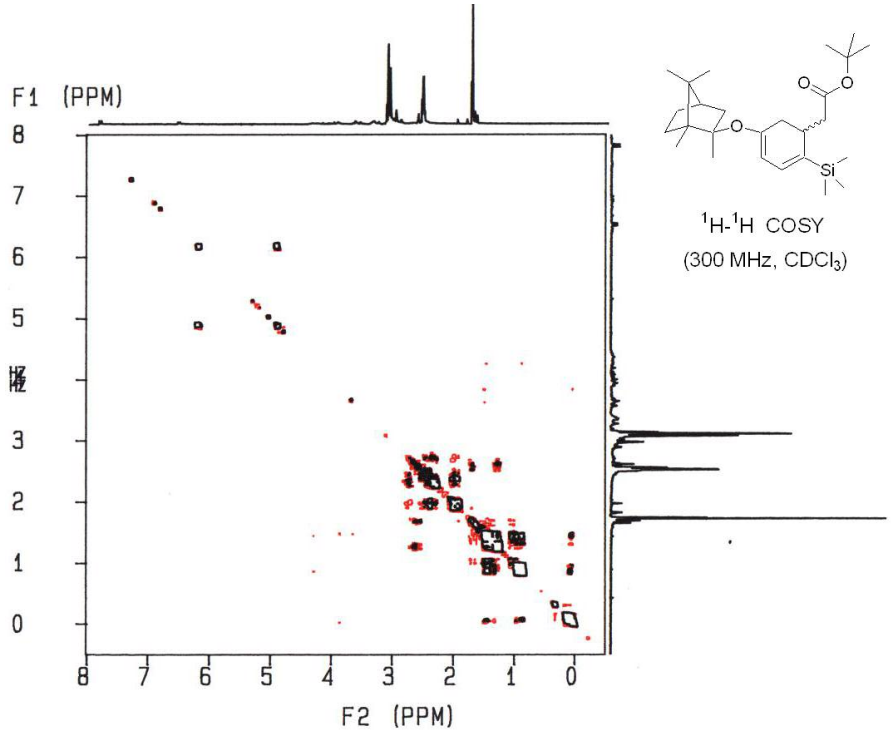
^{1}H NMR (300 MHz, CDCl$_3$) and ^{13}C NMR (75 MHz, CDCl$_3$) of **5a**



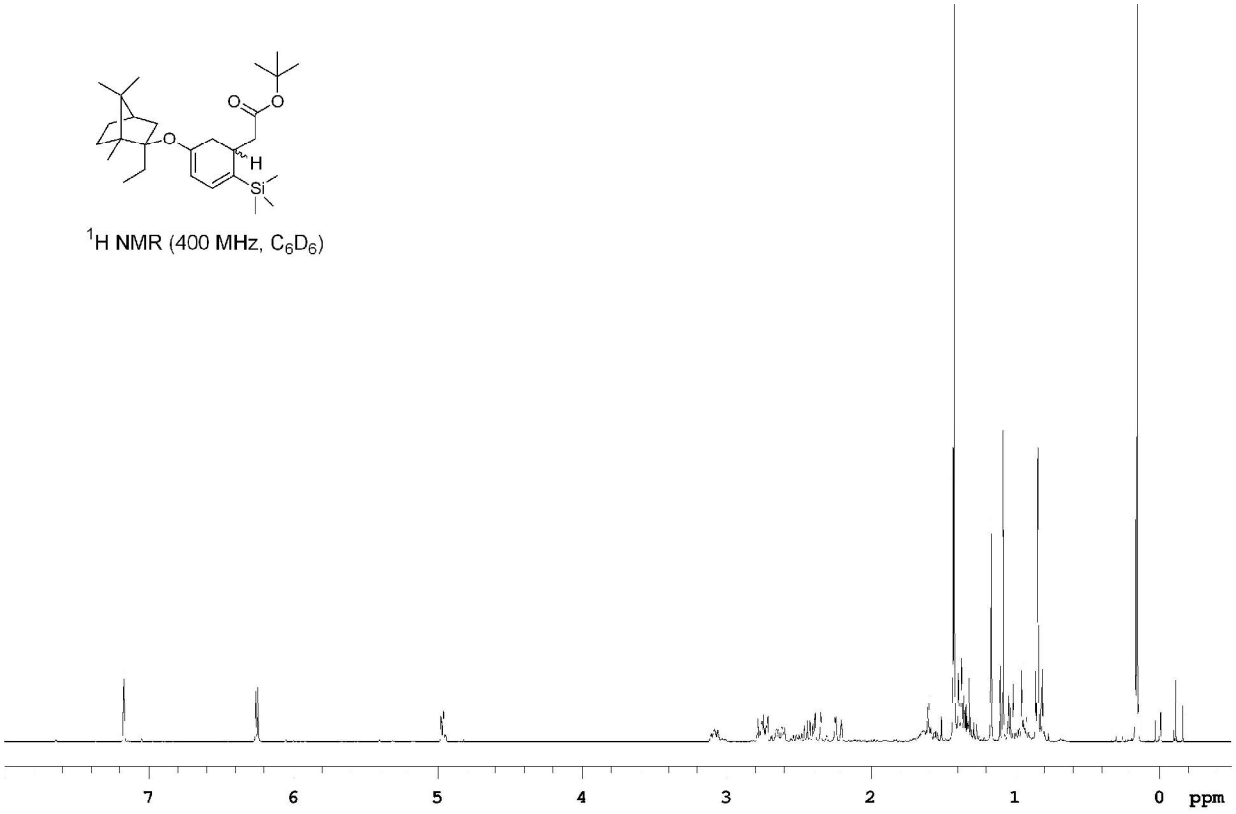


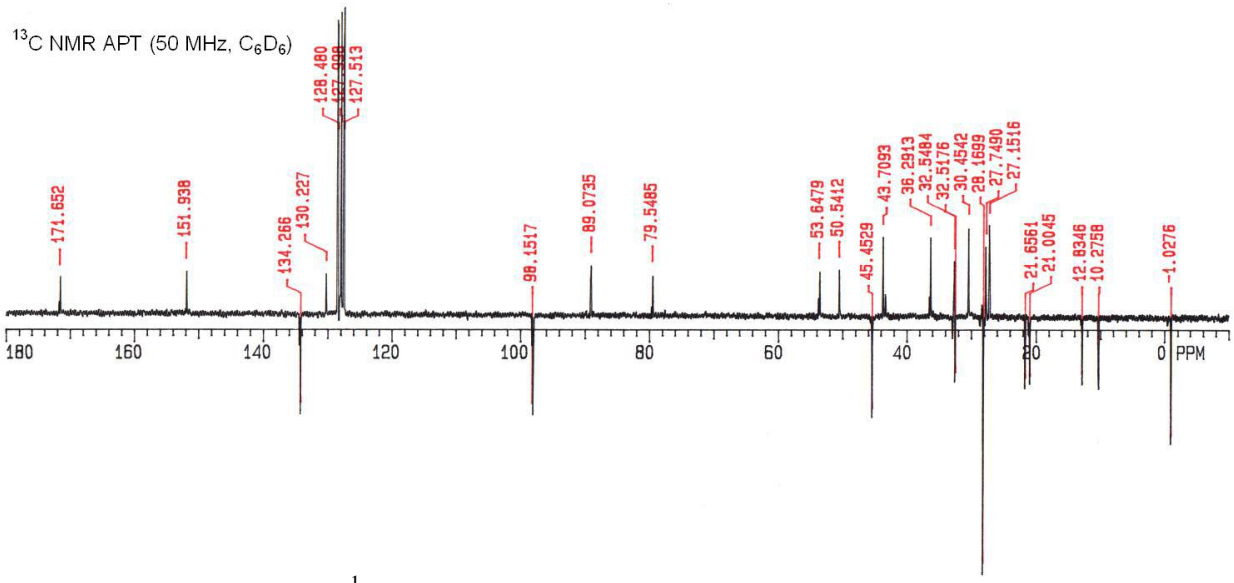
^{1}H NMR (300 MHz, $CDCl_3$) and ^{1}H-^{1}H COSY (300 MHz, $CDCl_3$) of **5b**



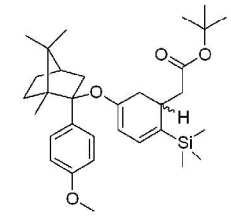


^{1}H NMR (400 MHz, C_6D_6) and ^{13}C APT NMR (50 MHz, C_6D_6) of **5g**



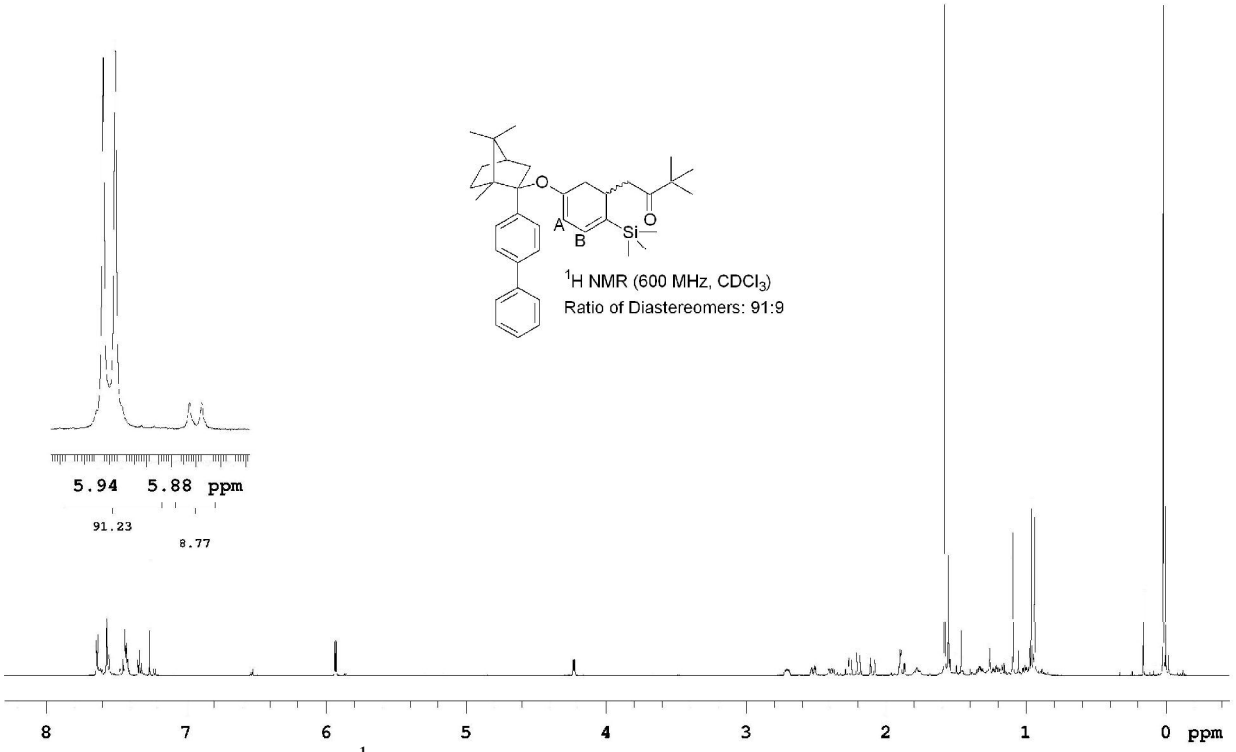


^{1}H NMR (300 MHz, $CDCl_3$) of **5e**

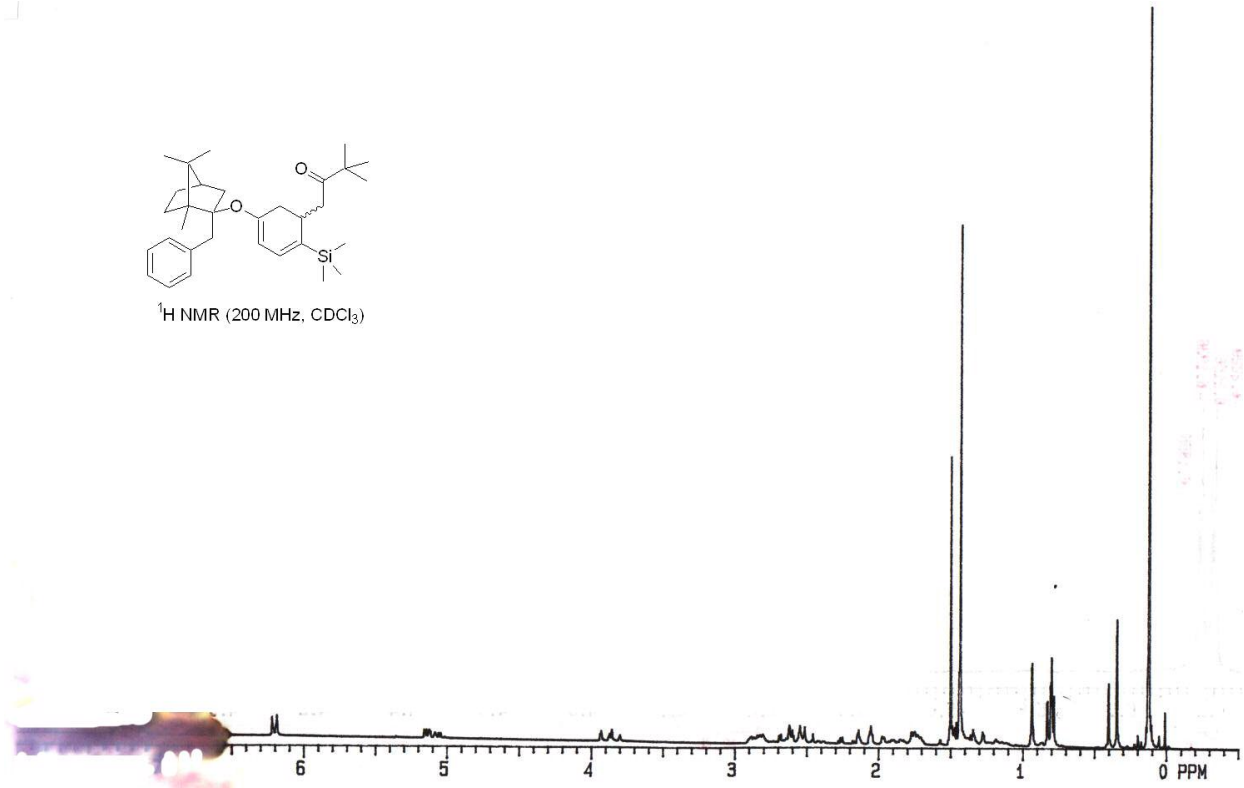


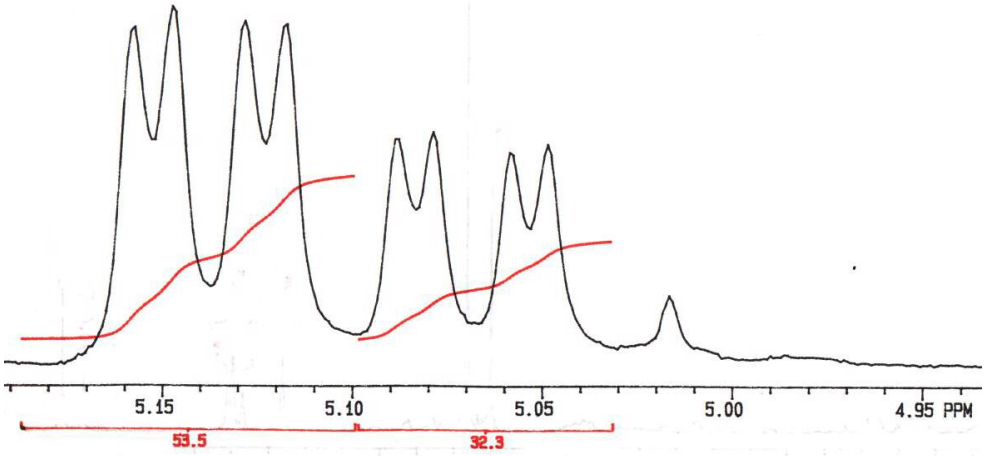
^{1}H NMR (300 MHz, $CDCl_3$)

^{1}H NMR (600 MHz, $CDCl_3$) of **5f**

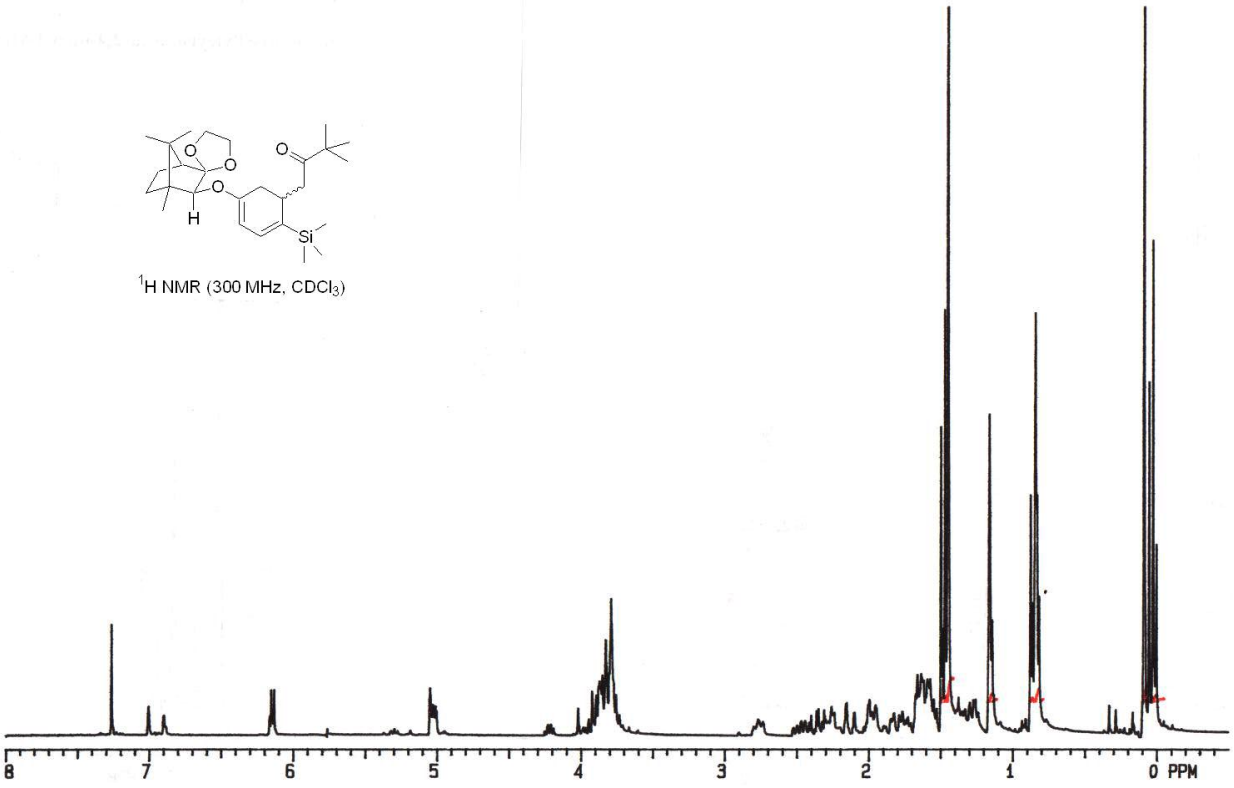


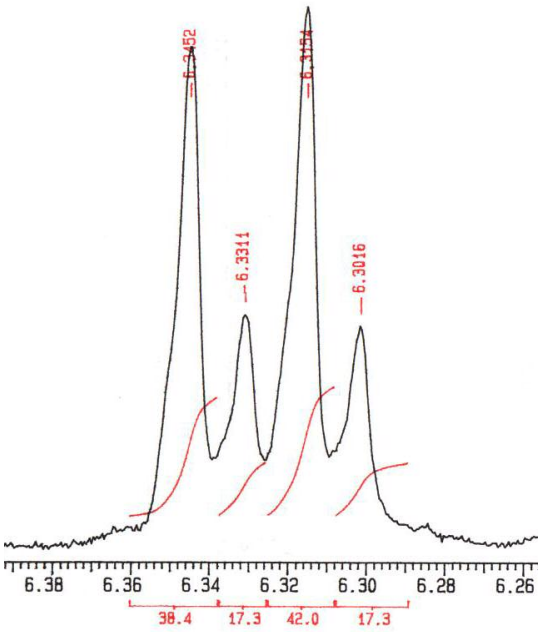
^{1}H NMR (200 MHz, $CDCl_3$) of **5d**



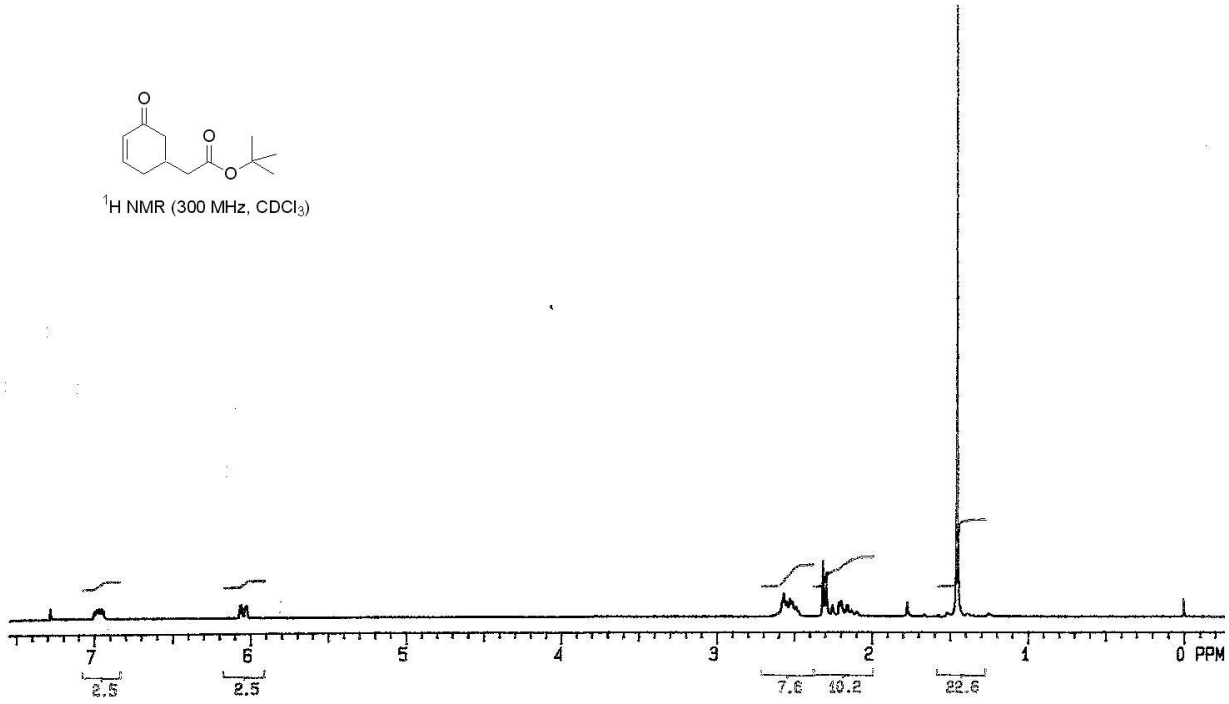


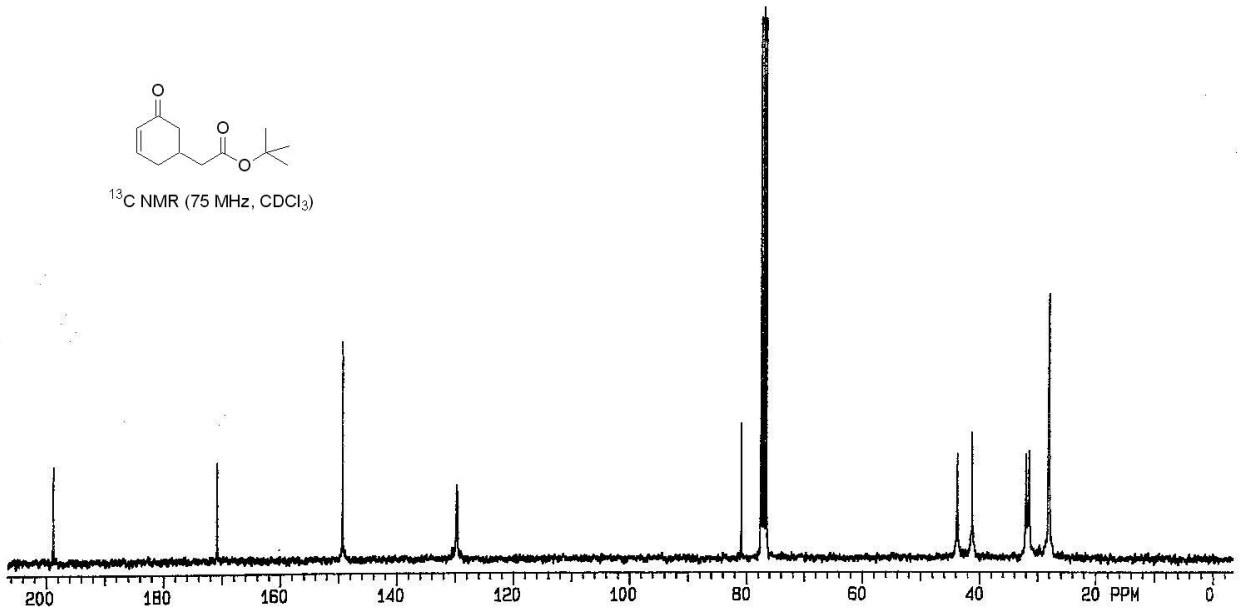
^{1}H NMR (300 MHz, $CDCl_3$) of **5c**



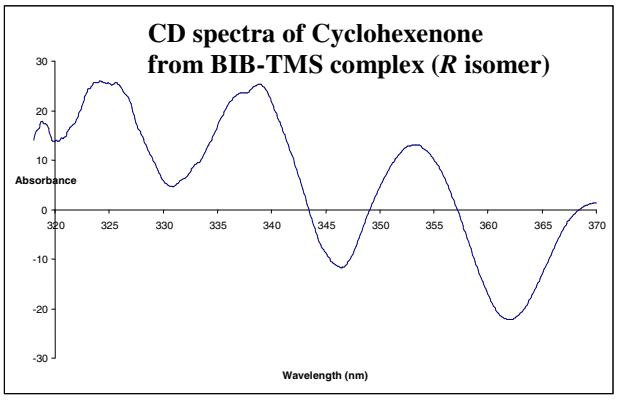


^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75MHz, $CDCl_3$) of **6**

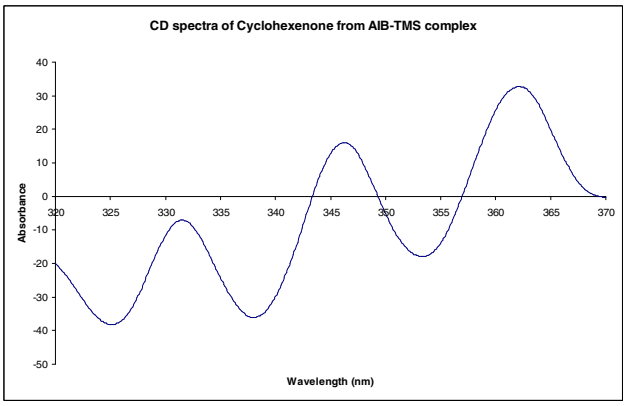




CD Spectrum of Major *R* isomer of **5**



CD Spectrum of Major *S* isomer of **5**


CD spectra of Cyclohexenone from AIB-TMS complex
Absorbance
Wavelength (nm)
40
30
20
10
0
-10
-20
-30
-40
-50
320
325
330
335
340
345
350
355
360
365
370

Crystallographic data for 3a, 3b and 3c in CIF format follow.

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 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
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 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
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 '-x+1/2, -y, z+1/2'
 '-x, y+1/2, -z+1/2'
 'x+1/2, -y+1/2, -z'

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The decay correction was applied simultaneously with the absorption correction
 in sadabs. No formal measure of the extent of decay is printed out by this
program.
The final unit cell is obtained from the refinement
 of the XYZ weighted centroids of reflections above 20 \s(I).
;

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_refine_special_details
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 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
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 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
;

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O1 O 0.29945(14) 0.83672(12) 0.87972(6) 0.0186(4) Uani 1.000000 1 d .
O2 O 0.61878(18) 0.68352(15) 0.91449(8) 0.0435(5) Uani 1.000000 1 d .
O3 O 0.72892(17) 1.01318(16) 0.82733(8) 0.0369(5) Uani 1.000000 1 d .
O4 O 0.79338(16) 0.93507(17) 1.01363(7) 0.0364(5) Uani 1.000000 1 d .
C1 C 0.5955(3) 1.3729(2) 0.98205(13) 0.0322(7) Uani 1.000000 1 d .
C2 C 0.6697(3) 1.1897(3) 1.08034(12) 0.0320(7) Uani 1.000000 1 d .
C3 C 0.4083(3) 1.2942(3) 1.07848(12) 0.0351(7) Uani 1.000000 1 d .
C4 C 0.3612(2) 0.9290(2) 0.90856(9) 0.0163(5) Uani 1.000000 1 d .
C5 C 0.3813(2) 0.9082(2) 0.97153(10) 0.0194(5) Uani 1.000000 1 d .
C6 C 0.4371(2) 1.00094(19) 1.00697(10) 0.0201(5) Uani 1.000000 1 d .
C7 C 0.4801(2) 1.11446(19) 0.98176(9) 0.0171(5) Uani 1.000000 1 d .
C8 C 0.4665(2) 1.1278(2) 0.91904(10) 0.0187(5) Uani 1.000000 1 d .
C9 C 0.4082(2) 1.0362(2) 0.88241(10) 0.0179(5) Uani 1.000000 1 d .
C10 C 0.2482(2) 0.85750(19) 0.81887(9) 0.0165(5) Uani 1.000000 1 d .
C11 C 0.3579(2) 0.8593(2) 0.77481(10) 0.0191(5) Uani 1.000000 1 d .
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C12 C 0.3620(3) 0.9352(2) 0.72383(11) 0.0268(6) Uani 1.000000 1 d .
C13 C 0.4652(3) 0.9351(2) 0.68604(12) 0.0358(7) Uani 1.000000 1 d .
C14 C 0.5647(3) 0.8590(3) 0.69765(12) 0.0388(7) Uani 1.000000 1 d .
C15 C 0.5617(3) 0.7815(2) 0.74697(12) 0.0329(6) Uani 1.000000 1 d .
C16 C 0.4591(2) 0.7813(2) 0.78508(11) 0.0247(6) Uani 1.000000 1 d .
C17 C 0.1547(2) 0.7475(2) 0.80923(9) 0.0175(5) Uani 1.000000 1 d .
C18 C 0.1160(2) 0.7535(2) 0.74197(10) 0.0244(6) Uani 1.000000 1 d .
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C20 C 0.0306(2) 0.9162(2) 0.80460(11) 0.0258(6) Uani 1.000000 1 d .
C21 C 0.1598(2) 0.9718(2) 0.81840(12) 0.0207(5) Uani 1.000000 1 d .
C22 C 0.0323(2) 0.7948(2) 0.84073(10) 0.0223(5) Uani 1.000000 1 d .
C23 C 0.0376(3) 0.8125(3) 0.90958(11) 0.0309(7) Uani 1.000000 1 d .
C24 C -0.0820(3) 0.7120(2) 0.82912(14) 0.0326(6) Uani 1.000000 1 d .
C25 C 0.2027(3) 0.6206(2) 0.82768(12) 0.0243(6) Uani 1.000000 1 d .
C26 C 0.5978(2) 0.7878(2) 0.92100(10) 0.0265(6) Uani 1.000000 1 d .
C27 C 0.7045(2) 0.9452(2) 0.98386(10) 0.0238(5) Uani 1.000000 1 d .
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H1B H 0.521(3) 1.410(2) 0.9639(11) 0.050 Uiso 1.000000 1 d .
H1C H 0.649(3) 1.352(2) 0.9511(12) 0.050 Uiso 1.000000 1 d .
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H2B H 0.750(3) 1.180(2) 1.0586(12) 0.050 Uiso 1.000000 1 d .
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H3B H 0.381(2) 1.224(2) 1.1044(12) 0.050 Uiso 1.000000 1 d .
H3C H 0.339(3) 1.320(2) 1.0561(12) 0.050 Uiso 1.000000 1 d .
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H16A H 0.460(2) 0.729(2) 0.8187(11) 0.050 Uiso 1.000000 1 d .
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O1 0.0249(9) 0.0162(8) 0.0147(8) -0.0009(6) -0.0039(7) -0.0030(7)
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C7 0.0176(13) 0.0161(12) 0.0175(12) -0.0029(9) 0.0005(10) 0.0018(10)
C8 0.0184(13) 0.0165(11) 0.0212(13) -0.0009(9) 0.0005(10) 0.0012(10)
C9 0.0229(13) 0.0163(11) 0.0147(11) 0.0017(10) -0.0008(10) 0.0040(11)
C10 0.0225(13) 0.0148(11) 0.0123(12) 0.0001(9) -0.0034(10) 0.0021(10)
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C26 0.0235(14) 0.0274(14) 0.0285(14) 0.0013(11) 0.0001(11) -0.0011(11)
C27 0.0258(14) 0.0224(13) 0.0233(13) 0.0014(11) 0.0050(11) -0.0003(12)
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 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix.  The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry.  An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.
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Si C1 1.852(3) . ?
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O1 C4 1.356(2) . ?
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C3 Si C7 106.00(12) . . ?
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Cr C4 C5 68.47(13) . . ?
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The final unit cell is obtained from the refinement
 of the XYZ weighted centroids of reflections above 20 \s(I).
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_diffrn_radiation_monochromator    graphite
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_diffrn_standards_decay_%         0.00
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_reflns_number_total              4724
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_reflns_threshold_expression      >2sigma(I)

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_computing_data_reduction          'Siemens SAINT'
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_refine_special_details
;
 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
;

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_refine_ls_matrix_type            full
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_refine_ls_weighting_details
 'calc w=1/[\s^2^(Fo^2^)+(0.0000P)^2^+2.4693P] where P=(Fo^2^+2Fc^2^)/3'
_atom_sites_solution_primary      direct
_atom_sites_solution_secondary    difmap
_atom_sites_solution_hydrogens      difmap
_refine_ls_hydrogen_treatment     mixed
_refine_ls_extinction_method      none
_refine_ls_extinction_coef        ?
_refine_ls_abs_structure_details
 'Flack H D (1983), Acta Cryst. A39, 876-881'
_refine_ls_abs_structure_Flack    0.07(3)
_refine_ls_number_reflns          4724
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Si Si -0.05120(15) 0.32258(11) 0.45878(8) 0.0194(2) Uani 1 1 d . . .
O4 O 0.5448(4) 0.2836(4) 0.1999(2) 0.0317(7) Uani 1 1 d . . .
O3 O 0.4259(5) 0.4762(3) 0.4265(2) 0.0330(8) Uani 1 1 d . . .
C28 C 0.3535(6) 0.3991(4) 0.3760(3) 0.0205(9) Uani 1 1 d . . .
O2 O 0.0397(6) 0.4656(4) 0.1637(3) 0.0463(11) Uani 1 1 d . . .
C18 C 0.3947(7) -0.1789(5) 0.0153(3) 0.0288(10) Uani 1 1 d . . .
H18B H 0.355(6) -0.111(4) -0.035(3) 0.020 Uiso 1 1 d . . .
H18A H 0.511(6) -0.213(5) 0.001(3) 0.020 Uiso 1 1 d . . .
C27 C 0.4271(5) 0.2814(5) 0.2358(3) 0.0216(8) Uani 1 1 d . . .
O1 O 0.3444(4) -0.0001(3) 0.22971(19) 0.0189(6) Uani 1 1 d . . .
C26 C 0.1199(6) 0.3919(4) 0.2143(3) 0.0246(10) Uani 1 1 d . . .
C1 C -0.1360(7) 0.4599(4) 0.3846(4) 0.0297(10) Uani 1 1 d . . .
H1C H -0.206(6) 0.512(5) 0.417(3) 0.020 Uiso 1 1 d . . .
H1B H -0.193(6) 0.436(5) 0.325(4) 0.020 Uiso 1 1 d . . .
H1A H -0.034(7) 0.503(5) 0.379(3) 0.020 Uiso 1 1 d . . .
C25 C 0.6217(7) -0.0987(5) 0.1647(4) 0.0313(11) Uani 1 1 d . . .
H25C H 0.642(6) -0.023(5) 0.136(3) 0.020 Uiso 1 1 d . . .
H25B H 0.698(7) -0.158(5) 0.166(3) 0.020 Uiso 1 1 d . . .
H25A H 0.647(6) -0.077(4) 0.234(4) 0.020 Uiso 1 1 d . . .
C6 C 0.2381(5) 0.1689(4) 0.4263(3) 0.0157(8) Uani 1 1 d . . .
H6 H 0.296(6) 0.186(4) 0.488(3) 0.020 Uiso 1 1 d . . .
C11 C 0.2737(7) 0.0625(4) 0.0622(3) 0.0234(9) Uani 1 1 d . . .
H11C H 0.402(7) 0.095(4) 0.064(3) 0.020 Uiso 1 1 d . . .
H11B H 0.207(6) 0.125(5) 0.079(3) 0.020 Uiso 1 1 d . . .
H11A H 0.223(6) 0.038(4) 0.003(4) 0.020 Uiso 1 1 d . . .
C8 C -0.0149(5) 0.1881(4) 0.2917(3) 0.0168(8) Uani 1 1 d . . .
H8 H -0.126(7) 0.213(4) 0.264(3) 0.020 Uiso 1 1 d . . .
C3 C -0.2397(6) 0.2389(5) 0.4872(4) 0.0312(11) Uani 1 1 d . . .
H3C H -0.310(6) 0.297(4) 0.528(3) 0.020 Uiso 1 1 d . . .
H3B H -0.218(6) 0.168(5) 0.517(3) 0.020 Uiso 1 1 d . . .
H3A H -0.325(6) 0.208(4) 0.432(3) 0.020 Uiso 1 1 d . . .
C21 C 0.1148(6) -0.1259(4) 0.1166(4) 0.0240(9) Uani 1 1 d . . .
H21B H 0.068(6) -0.118(4) 0.171(4) 0.020 Uiso 1 1 d . . .
H21A H 0.018(6) -0.099(4) 0.065(3) 0.020 Uiso 1 1 d . . .
C9 C 0.0711(6) 0.1135(4) 0.2338(3) 0.0186(8) Uani 1 1 d . . .
H9 H 0.037(7) 0.111(5) 0.177(4) 0.020 Uiso 1 1 d . . .
C2 C 0.1095(7) 0.3669(6) 0.5722(4) 0.0353(12) Uani 1 1 d . . .
H2C H 0.057(6) 0.419(5) 0.609(3) 0.020 Uiso 1 1 d . . .
H2B H 0.208(7) 0.408(5) 0.562(3) 0.020 Uiso 1 1 d . . .
H2A H 0.156(6) 0.290(5) 0.611(3) 0.020 Uiso 1 1 d . . .
C20 C 0.1808(7) -0.2563(4) 0.0987(4) 0.0277(11) Uani 1 1 d . . .
H20 H 0.111(7) -0.306(5) 0.104(4) 0.020 Uiso 1 1 d . . .
C7 C 0.0641(5) 0.2163(4) 0.3878(3) 0.0172(8) Uani 1 1 d . . .
C5 C 0.3248(6) 0.0958(4) 0.3707(3) 0.0179(8) Uani 1 1 d . . .
H5 H 0.434(7) 0.069(5) 0.397(4) 0.020 Uiso 1 1 d . . .
C4 C 0.2425(5) 0.0680(3) 0.2739(3) 0.0149(8) Uani 1 1 d . . .
C23 C 0.3662(7) -0.2551(4) 0.2743(3) 0.0284(11) Uani 1 1 d . . .
H23C H 0.326(6) -0.328(5) 0.286(3) 0.020 Uiso 1 1 d . . .
H23B H 0.287(6) -0.205(5) 0.294(3) 0.020 Uiso 1 1 d . . .
H23A H 0.489(6) -0.240(5) 0.318(3) 0.020 Uiso 1 1 d . . .
C10 C 0.2857(5) -0.0467(4) 0.1305(3) 0.0166(8) Uani 1 1 d . . .
C17 C 0.4316(6) -0.1415(4) 0.1234(3) 0.0222(9) Uani 1 1 d . . .
C24 C 0.4753(9) -0.3752(5) 0.1558(4) 0.0389(13) Uani 1 1 d . . .
H24C H 0.436(7) -0.441(5) 0.168(4) 0.020 Uiso 1 1 d . . .
H24B H 0.578(7) -0.372(5) 0.197(4) 0.020 Uiso 1 1 d . . .
H24A H 0.500(6) -0.397(4) 0.089(4) 0.020 Uiso 1 1 d . . .
C19 C 0.2235(8) -0.2542(4) -0.0001(4) 0.0383(13) Uani 1 1 d . . .
H19B H 0.237(6) -0.326(5) -0.023(3) 0.020 Uiso 1 1 d . . .
H19A H 0.119(6) -0.225(5) -0.048(3) 0.020 Uiso 1 1 d . . .
C22 C 0.3666(6) -0.2593(4) 0.1683(3) 0.0233(9) Uani 1 1 d . . .

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Si 0.0181(6) 0.0237(6) 0.0167(5) -0.0034(4) 0.0048(4) 0.0001(4)
O4 0.0293(16) 0.0364(18) 0.0329(16) -0.0057(17) 0.0144(13) -0.0032(17)
O3 0.0350(19) 0.0286(19) 0.0327(19) -0.0086(15) 0.0028(15) -0.0049(15)
C28 0.022(2) 0.020(2) 0.017(2) 0.0004(17) -0.0008(16) 0.0019(17)
O2 0.050(2) 0.030(2) 0.048(2) 0.0167(18) -0.0119(18) -0.0016(17)
C18 0.047(3) 0.032(2) 0.0048(17) -0.0048(17) 0.0015(17) 0.008(2)
C27 0.026(2) 0.0157(18) 0.0213(18) -0.0009(19) 0.0034(15) 0.003(2)
O1 0.0220(15) 0.0188(15) 0.0147(13) -0.0030(11) 0.0022(11) 0.0033(12)
C26 0.023(2) 0.018(2) 0.026(2) 0.0052(18) -0.0061(18) -0.0041(17)
C1 0.035(3) 0.018(2) 0.037(3) -0.005(2) 0.011(2) 0.000(2)
C25 0.028(3) 0.030(3) 0.040(3) 0.002(2) 0.015(2) 0.004(2)
C6 0.020(2) 0.0157(19) 0.0125(18) 0.0012(15) 0.0060(15) -0.0028(15)
C11 0.032(3) 0.018(2) 0.020(2) 0.0015(17) 0.0045(18) 0.0006(18)
C8 0.0124(19) 0.017(2) 0.021(2) -0.0006(15) 0.0039(15) -0.0013(15)
C3 0.019(2) 0.042(3) 0.034(3) 0.008(2) 0.0093(19) -0.0003(19)
C21 0.022(2) 0.020(2) 0.028(2) -0.0043(17) 0.0035(18) -0.0006(17)
C9 0.021(2) 0.014(2) 0.021(2) 0.0000(16) 0.0043(17) -0.0033(16)
C2 0.026(3) 0.045(3) 0.032(3) -0.016(2) 0.002(2) 0.000(2)
C20 0.033(3) 0.015(2) 0.035(3) -0.0016(17) 0.007(2) -0.0069(17)
C7 0.022(2) 0.0112(18) 0.020(2) -0.0015(15) 0.0094(16) -0.0022(16)
C5 0.024(2) 0.0100(19) 0.021(2) 0.0028(15) 0.0068(17) -0.0021(16)
C4 0.018(2) 0.0106(18) 0.0179(19) 0.0008(14) 0.0080(15) -0.0007(14)
C23 0.040(3) 0.021(3) 0.027(2) 0.0077(17) 0.013(2) 0.0085(19)
C10 0.020(2) 0.017(2) 0.0142(18) -0.0017(15) 0.0057(15) -0.0015(16)
C17 0.024(2) 0.019(2) 0.023(2) -0.0023(17) 0.0071(17) 0.0034(17)
C24 0.056(4) 0.024(3) 0.037(3) 0.002(2) 0.014(3) 0.012(3)
C19 0.060(4) 0.020(3) 0.030(3) -0.0116(19) 0.001(2) 0.002(2)
C22 0.026(2) 0.012(2) 0.033(2) 0.0021(16) 0.0104(18) 0.0057(15)

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;
 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix.  The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry.  An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.
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Cr C26 1.840(4) . ?
Cr C27 1.849(4) . ?
Cr C8 2.194(4) . ?
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Cr C7 2.210(4) . ?
Cr C5 2.246(4) . ?
Cr C9 2.264(4) . ?
Cr C4 2.288(4) . ?
Si C3 1.848(5) . ?
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Si C2 1.859(5) . ?
Si C1 1.864(5) . ?
Si C7 1.902(4) . ?
O4 C27 1.150(5) . ?
O3 C28 1.164(5) . ?
O2 C26 1.159(6) . ?
C18 C19 1.530(8) . ?
C18 C17 1.562(6) . ?
O1 C4 1.348(5) . ?
O1 C10 1.476(5) . ?
C25 C17 1.522(7) . ?
C6 C5 1.408(6) . ?
C6 C7 1.425(6) . ?
C11 C10 1.531(6) . ?
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C8 C9 1.436(6) . ?
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C28 Cr C27 88.1(2) . . ?
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C5 Cr C9 65.15(16) . . ?
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C28 Cr C4 143.17(17) . . ?
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C27 Cr C4 86.57(19) . . ?
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C7 Cr C4 79.51(14) . . ?
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C3 Si C2 109.5(3) . . ?
C3 Si C1 109.6(2) . . ?
C2 Si C1 111.1(3) . . ?
C3 Si C7 108.3(2) . . ?
C2 Si C7 109.0(2) . . ?
C1 Si C7 109.4(2) . . ?
O3 C28 Cr 179.0(4) . . ?
C19 C18 C17 103.3(4) . . ?
O4 C27 Cr 178.1(4) . . ?
C4 O1 C10 124.3(3) . . ?
O2 C26 Cr 178.3(5) . . ?
C5 C6 C7 121.4(4) . . ?
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C8 C7 C6 116.8(4) . . ?
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Si C7 Cr 125.3(2) . . ?
C6 C5 C4 120.9(4) . . ?
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O1 C4 C5 113.8(4) . . ?
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C5 C4 Cr 70.2(2) . . ?
O1 C10 C11 107.8(3) . . ?
O1 C10 C17 103.5(3) . . ?
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C25 C17 C22 117.7(4) . . ?
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C23 C22 C24 105.7(4) . . ?
C20 C22 C24 112.9(4) . . ?
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C23 C22 C17 117.4(4) . . ?
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_exptl_crystal_density_method      'not measured'
_exptl_crystal_F_000               1048
_exptl_absorpt_coefficient_mu      0.553
_exptl_absorpt_correction_type      'Empirical :Multipole Expansion (Blessing,
1995)'
_exptl_absorpt_correction_T_min    0.924428
_exptl_absorpt_correction_T_max    1.000000
_exptl_absorpt_process_details     ?

_exptl_special_details
;
The decay correction was applied simultaneously with the absorption correction
 in sadabs. No formal measure of the extent of decay is printed out by this
program.
The final unit cell is obtained from the refinement
 of the XYZ weighted centroids of reflections above 20 \s(I).
;

_diffrn_ambient_temperature        150(1)
_diffrn_radiation_wavelength        0.71073
_diffrn_radiation_type              MoK\a
_diffrn_radiation_source            'Sealed Tube'
_diffrn_radiation_monochromator     graphite
_diffrn_measurement_device_type    'Platform Diffractometer'
_diffrn_measurement_method          '\w scans'
_diffrn_detector_area_resol_mean   ?
_diffrn_standards_number           ?
_diffrn_standards_interval_count   ?
_diffrn_standards_interval_time    ?
_diffrn_standards_decay_%          0.00
_diffrn_reflns_number              22225
_diffrn_reflns_av_R_equivalents    0.0519
_diffrn_reflns_av_sigmaI/netI      0.0785
_diffrn_reflns_limit_h_min         -11
_diffrn_reflns_limit_h_max         11
_diffrn_reflns_limit_k_min         -13
_diffrn_reflns_limit_k_max         13
_diffrn_reflns_limit_l_min         -32
_diffrn_reflns_limit_l_max         31
_diffrn_reflns_theta_min           3.14
_diffrn_reflns_theta_max           26.56
_reflns_number_total               9263
_reflns_number_gt                  8142
_reflns_threshold_expression       >2sigma(I)

_computing_data_collection          'Siemens SMART'
_computing_cell_refinement          'Siemens SAINT'
_computing_data_reduction           'Siemens SAINT'
_computing_structure_solution      'SHELXS-97 (Sheldrick, 1990)'
_computing_structure_refinement    'SHELXL-97 (Sheldrick, 1997)'
_computing_molecular_graphics       'Siemens SHELXTL'
_computing_publication_material     'Siemens SHELXTL and the Toledo cifomatic'
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_refine_special_details
;
 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
;

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_refine_ls_matrix_type            full
_refine_ls_weighting_scheme       calc
_refine_ls_weighting_details
 'calc w=1/[\s^2^(Fo^2^)+(0.0192P)^2^+5.6596P] where P=(Fo^2^+2Fc^2^)/3'
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_atom_sites_solution_secondary    difmap
_atom_sites_solution_hydrogens      difmap
_refine_ls_hydrogen_treatment     mixed
_refine_ls_extinction_method      none
_refine_ls_extinction_coef        ?
_refine_ls_abs_structure_details
 'Flack H D (1983), Acta Cryst. A39, 876-881'
_refine_ls_abs_structure_Flack    0.01(2)
_refine_ls_number_reflns          9263
_refine_ls_number_parameters      770
_refine_ls_number_restraints      1
_refine_ls_R_factor_all           0.0743
_refine_ls_R_factor_gt            0.0631
_refine_ls_wR_factor_ref          0.1173
_refine_ls_wR_factor_gt           0.1130
_refine_ls_goodness_of_fit_ref    1.077
_refine_ls_restrained_S_all       1.077
_refine_ls_shift/su_max           0.046
_refine_ls_shift/su_mean          0.002

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Cr1 Cr -0.24266(8) -0.44765(8) -0.08902(3) 0.01323(18) Uani 1.000000 1 d .
Cr1' Cr 0.33095(9) -0.83030(8) -0.40387(3) 0.01500(19) Uani 1.000000 1 d .
Si1 Si -0.59512(15) -0.43788(16) -0.02374(5) 0.0186(3) Uani 1.000000 1 d .
Si1' Si -0.05092(16) -0.87825(14) -0.46961(6) 0.0184(3) Uani 1.000000 1 d .
O1 O -0.1049(4) -0.7272(4) -0.11869(13) 0.0189(8) Uani 1.000000 1 d .
O1' O 0.4616(4) -0.5379(4) -0.38535(13) 0.0206(9) Uani 1.000000 1 d .
O2 O -0.3722(5) -0.1990(4) -0.12523(17) 0.0422(12) Uani 1.000000 1 d .
O2' O 0.2732(5) -1.0305(4) -0.32641(19) 0.0410(12) Uani 1.000000 1 d .
O3 O -0.0522(5) -0.3139(5) -0.00391(17) 0.0441(12) Uani 1.000000 1 d .
O3' O 0.4113(5) -1.0251(5) -0.48018(18) 0.0437(12) Uani 1.000000 1 d .
O4 O -0.0064(5) -0.4049(5) -0.16021(18) 0.0461(13) Uani 1.000000 1 d .
O4' O 0.6511(4) -0.8377(5) -0.36087(15) 0.0410(11) Uani 1.000000 1 d .
```

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O5 O -0.3139(4) -0.7981(3) -0.23618(13) 0.0187(8) Uani 1.000000 1 d .
O5' O 0.3508(5) -0.4700(4) -0.26323(16) 0.0345(11) Uani 1.000000 1 d .
O6 O -0.3014(4) -0.8991(3) -0.15864(13) 0.0183(8) Uani 1.000000 1 d .
O6' O 0.2925(4) -0.3721(4) -0.34068(17) 0.0340(11) Uani 1.000000 1 d .
C1 C -0.6782(7) -0.3124(7) -0.0678(2) 0.0293(14) Uani 1.000000 1 d .
C1' C 0.0014(7) -0.9358(7) -0.5336(2) 0.0317(15) Uani 1.000000 1 d .
C2 C -0.5093(8) -0.3770(7) 0.0401(2) 0.0341(16) Uani 1.000000 1 d .
C2' C -0.0761(8) -1.0091(7) -0.4237(3) 0.0325(15) Uani 1.000000 1 d .
C3 C -0.7407(8) -0.5549(7) -0.0118(3) 0.0348(16) Uani 1.000000 1 d .
C3' C -0.2226(7) -0.7825(7) -0.4815(3) 0.0354(16) Uani 1.000000 1 d .
C4 C -0.2171(6) -0.6592(5) -0.10225(19) 0.0147(11) Uani 1.000000 1 d .
C4' C 0.3456(6) -0.6152(5) -0.3990(2) 0.0156(11) Uani 1.000000 1 d .
C5 C -0.2025(6) -0.6317(5) -0.0485(2) 0.0176(12) Uani 1.000000 1 d .
C5' C 0.3342(6) -0.6550(5) -0.4518(2) 0.0167(11) Uani 1.000000 1 d .
C6 C -0.3150(6) -0.5646(5) -0.0263(2) 0.0152(11) Uani 1.000000 1 d .
C6' C 0.2160(6) -0.7323(5) -0.4711(2) 0.0190(12) Uani 1.000000 1 d .
C7 C -0.4449(6) -0.5215(5) -0.05645(19) 0.0139(11) Uani 1.000000 1 d .
C7' C 0.1055(6) -0.7746(5) -0.4402(2) 0.0168(11) Uani 1.000000 1 d .
C8 C -0.4525(6) -0.5449(5) -0.1107(2) 0.0152(11) Uani 1.000000 1 d .
C8' C 0.1267(6) -0.7372(5) -0.3873(2) 0.0181(12) Uani 1.000000 1 d .
C9 C -0.3428(5) -0.6122(5) -0.13419(19) 0.0123(11) Uani 1.000000 1 d .
C9' C 0.2432(6) -0.6591(5) -0.3660(2) 0.0173(11) Uani 1.000000 1 d .
C10 C -0.1003(6) -0.7511(5) -0.1735(2) 0.0180(12) Uani 1.000000 1 d .
C10' C 0.5089(6) -0.5142(5) -0.33121(19) 0.0159(11) Uani 1.000000 1 d .
C17 C 0.0524(5) -0.8059(5) -0.1820(2) 0.0197(12) Uani 1.000000 1 d .
C17' C 0.6646(5) -0.4532(6) -0.32685(19) 0.0203(11) Uani 1.000000 1 d .
C18 C 0.0599(7) -0.7989(6) -0.2414(2) 0.0273(14) Uani 1.000000 1 d .
C18' C 0.7195(7) -0.4591(7) -0.2682(2) 0.0276(13) Uani 1.000000 1 d .
C19 C -0.0492(6) -0.9022(6) -0.2652(2) 0.0275(14) Uani 1.000000 1 d .
C19' C 0.6302(7) -0.3558(6) -0.2433(2) 0.0272(14) Uani 1.000000 1 d .
C20 C -0.1110(6) -0.9550(6) -0.2166(2) 0.0210(12) Uani 1.000000 1 d .
C20' C 0.5263(6) -0.3075(6) -0.2903(2) 0.0248(13) Uani 1.000000 1 d .
C21 C -0.2128(5) -0.8520(5) -0.19641(19) 0.0176(12) Uani 1.000000 1 d .
C21' C 0.4138(6) -0.4128(5) -0.3059(2) 0.0213(12) Uani 1.000000 1 d .
C22 C 0.0262(5) -0.9519(6) -0.1750(2) 0.0201(11) Uani 1.000000 1 d .
C22' C 0.6297(6) -0.3098(6) -0.3347(2) 0.0235(13) Uani 1.000000 1 d .
C23 C -0.0013(8) -0.9936(7) -0.1199(2) 0.0315(15) Uani 1.000000 1 d .
C23' C 0.5549(9) -0.2724(7) -0.3891(3) 0.0390(17) Uani 1.000000 1 d .
C24 C 0.1558(8) -1.0318(7) -0.1907(3) 0.0358(17) Uani 1.000000 1 d .
C24' C 0.7677(8) -0.2252(7) -0.3245(3) 0.0318(15) Uani 1.000000 1 d .
C25 C 0.1814(6) -0.7455(7) -0.1495(3) 0.0342(16) Uani 1.000000 1 d .
C25' C 0.7681(8) -0.5160(8) -0.3618(3) 0.0380(17) Uani 1.000000 1 d .
C26 C -0.3243(6) -0.2955(5) -0.11165(19) 0.0178(12) Uani 1.000000 1 d .
C26' C 0.2945(6) -0.9548(6) -0.3567(2) 0.0257(12) Uani 1.000000 1 d .
C27 C -0.0972(6) -0.4220(5) -0.1330(2) 0.0263(14) Uani 1.000000 1 d .
C27' C 0.5272(6) -0.8349(6) -0.37734(19) 0.0225(12) Uani 1.000000 1 d .
C28 C -0.1252(6) -0.3641(5) -0.0377(2) 0.0232(13) Uani 1.000000 1 d .
C28' C 0.3791(6) -0.9507(7) -0.4505(2) 0.0268(13) Uani 1.000000 1 d .
C46 C -0.4468(9) -0.8683(9) -0.2360(3) 0.050(2) Uani 1.000000 1 d .
C46' C 0.2245(10) -0.3937(9) -0.2550(4) 0.069(3) Uani 1.000000 1 d .
C48 C -0.4404(7) -0.9333(7) -0.1859(2) 0.0289(14) Uani 1.000000 1 d .
C48' C 0.1747(8) -0.3433(9) -0.3102(4) 0.064(3) Uani 1.000000 1 d .
H1A H -0.711(7) -0.339(7) -0.100(3) 0.050 Uiso 1.000000 1 d .
H1B H -0.618(8) -0.246(7) -0.073(3) 0.050 Uiso 1.000000 1 d .
H1C H -0.764(8) -0.272(7) -0.058(3) 0.050 Uiso 1.000000 1 d .
H1D H -0.060(8) -0.990(7) -0.549(3) 0.050 Uiso 1.000000 1 d .
H1E H 0.115(8) -0.990(6) -0.531(3) 0.050 Uiso 1.000000 1 d .
H1F H 0.008(7) -0.862(7) -0.557(3) 0.050 Uiso 1.000000 1 d .
H2A H -0.444(8) -0.324(8) 0.038(3) 0.050 Uiso 1.000000 1 d .
H2B H -0.472(8) -0.433(8) 0.059(3) 0.050 Uiso 1.000000 1 d .
H2C H -0.577(7) -0.337(7) 0.059(2) 0.050 Uiso 1.000000 1 d .
H2D H -0.162(8) -1.059(7) -0.431(3) 0.050 Uiso 1.000000 1 d .
H2E H -0.084(7) -0.975(7) -0.392(3) 0.050 Uiso 1.000000 1 d .
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H2F H -0.005(8) -1.074(7) -0.425(3) 0.050 Uiso 1.000000 1 d .
H3A H -0.800(8) -0.597(7) -0.038(3) 0.050 Uiso 1.000000 1 d .
H3B H -0.813(8) -0.517(7) 0.009(3) 0.050 Uiso 1.000000 1 d .
H3C H -0.700(8) -0.619(7) 0.006(3) 0.050 Uiso 1.000000 1 d .
H3D H -0.309(7) -0.833(7) -0.502(2) 0.050 Uiso 1.000000 1 d .
H3E H -0.217(8) -0.729(7) -0.508(3) 0.050 Uiso 1.000000 1 d .
H3F H -0.239(8) -0.751(7) -0.455(3) 0.050 Uiso 1.000000 1 d .
H5A H -0.117(6) -0.646(5) -0.027(2) 0.020 Uiso 1.000000 1 d .
H5D H 0.406(6) -0.623(5) -0.472(2) 0.020 Uiso 1.000000 1 d .
H6A H -0.301(6) -0.545(5) 0.010(2) 0.020 Uiso 1.000000 1 d .
H6D H 0.210(6) -0.753(5) -0.504(2) 0.020 Uiso 1.000000 1 d .
H8A H -0.527(6) -0.515(5) -0.130(2) 0.020 Uiso 1.000000 1 d .
H8D H 0.060(6) -0.772(5) -0.368(2) 0.020 Uiso 1.000000 1 d .
H9A H -0.345(6) -0.625(5) -0.171(2) 0.020 Uiso 1.000000 1 d .
H9D H 0.251(6) -0.645(5) -0.330(2) 0.020 Uiso 1.000000 1 d .
H10A H -0.117(6) -0.687(6) -0.192(2) 0.020 Uiso 1.000000 1 d .
H10D H 0.509(6) -0.600(5) -0.312(2) 0.020 Uiso 1.000000 1 d .
H18A H 0.040(6) -0.715(6) -0.253(2) 0.020 Uiso 1.000000 1 d .
H18B H 0.156(6) -0.804(5) -0.2515(19) 0.020 Uiso 1.000000 1 d .
H18D H 0.697(6) -0.528(6) -0.253(2) 0.020 Uiso 1.000000 1 d .
H18E H 0.832(6) -0.454(6) -0.2574(19) 0.020 Uiso 1.000000 1 d .
H19A H -0.130(6) -0.860(5) -0.2914(19) 0.020 Uiso 1.000000 1 d .
H19B H -0.005(6) -0.969(5) -0.282(2) 0.020 Uiso 1.000000 1 d .
H19D H 0.563(6) -0.370(5) -0.220(2) 0.020 Uiso 1.000000 1 d .
H19E H 0.692(6) -0.292(5) -0.227(2) 0.020 Uiso 1.000000 1 d .
H20A H -0.164(6) -1.028(6) -0.220(2) 0.020 Uiso 1.000000 1 d .
H20D H 0.475(6) -0.212(5) -0.287(2) 0.020 Uiso 1.000000 1 d .
H23A H 0.080(8) -1.004(7) -0.099(3) 0.050 Uiso 1.000000 1 d .
H23B H -0.027(8) -1.084(8) -0.113(3) 0.050 Uiso 1.000000 1 d .
H23C H -0.074(8) -0.954(7) -0.104(3) 0.050 Uiso 1.000000 1 d .
H23D H 0.524(8) -0.169(7) -0.386(3) 0.050 Uiso 1.000000 1 d .
H23E H 0.456(8) -0.315(7) -0.399(2) 0.050 Uiso 1.000000 1 d .
H23F H 0.621(8) -0.296(7) -0.415(3) 0.050 Uiso 1.000000 1 d .
H24A H 0.245(8) -1.021(7) -0.161(3) 0.050 Uiso 1.000000 1 d .
H24B H 0.193(7) -1.009(6) -0.228(3) 0.050 Uiso 1.000000 1 d .
H24C H 0.141(8) -1.111(7) -0.188(3) 0.050 Uiso 1.000000 1 d .
H24D H 0.748(8) -0.134(7) -0.321(3) 0.050 Uiso 1.000000 1 d .
H24E H 0.834(8) -0.219(7) -0.360(3) 0.050 Uiso 1.000000 1 d .
H24F H 0.827(8) -0.239(7) -0.294(3) 0.050 Uiso 1.000000 1 d .
H25D H 0.794(8) -0.598(8) -0.351(3) 0.050 Uiso 1.000000 1 d .
H25D H 0.183(7) -0.647(7) -0.153(3) 0.050 Uiso 1.000000 1 d .
H25E H 0.854(8) -0.475(7) -0.353(3) 0.050 Uiso 1.000000 1 d .
H25E H 0.267(8) -0.771(7) -0.160(3) 0.050 Uiso 1.000000 1 d .
H25F H 0.737(8) -0.512(7) -0.398(3) 0.050 Uiso 1.000000 1 d .
H25F H 0.174(7) -0.748(7) -0.111(3) 0.050 Uiso 1.000000 1 d .
H46A H -0.446(7) -0.908(6) -0.263(2) 0.020 Uiso 1.000000 1 d .
H46B H -0.519(6) -0.842(6) -0.253(2) 0.020 Uiso 1.000000 1 d .
H46D H 0.284(6) -0.298(5) -0.239(2) 0.020 Uiso 1.000000 1 d .
H46E H 0.163(6) -0.456(6) -0.230(2) 0.020 Uiso 1.000000 1 d .
H48A H -0.506(6) -0.895(5) -0.163(2) 0.020 Uiso 1.000000 1 d .
H48B H -0.440(6) -1.015(6) -0.196(2) 0.020 Uiso 1.000000 1 d .
H48D H 0.104(6) -0.406(6) -0.325(2) 0.020 Uiso 1.000000 1 d .
H48E H 0.174(6) -0.261(6) -0.303(2) 0.020 Uiso 1.000000 1 d .

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Cr1 0.0145(4) 0.0116(4) 0.0136(4) -0.0015(4) 0.0016(3) -0.0008(4)
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Cr1' 0.0159(4) 0.0160(4) 0.0135(4) -0.0001(4) 0.0037(3) 0.0013(4)
Si1 0.0196(7) 0.0185(8) 0.0183(7) -0.0039(7) 0.0054(6) 0.0023(7)
Si1' 0.0184(8) 0.0185(8) 0.0183(7) -0.0026(6) 0.0028(6) -0.0040(6)
O1 0.0155(19) 0.023(2) 0.0176(18) -0.0019(16) 0.0001(15) 0.0100(16)
O1' 0.023(2) 0.025(2) 0.0136(19) -0.0013(16) 0.0052(15) -0.0131(17)
O2 0.064(3) 0.023(3) 0.040(3) 0.008(2) 0.005(2) 0.002(2)
O2' 0.049(3) 0.030(3) 0.047(3) 0.022(2) 0.017(2) 0.006(2)
O3 0.038(3) 0.046(3) 0.045(3) -0.017(2) -0.011(2) -0.014(2)
O3' 0.038(3) 0.049(3) 0.044(3) -0.020(2) 0.008(2) 0.011(2)
O4 0.039(3) 0.056(3) 0.048(3) -0.010(2) 0.026(2) -0.016(2)
O4' 0.022(2) 0.062(3) 0.036(2) -0.003(2) -0.0118(18) 0.005(2)
O5 0.0159(19) 0.025(2) 0.0152(18) 0.0012(15) -0.0006(14) 0.0002(16)
O5' 0.041(3) 0.033(3) 0.035(2) -0.009(2) 0.028(2) -0.013(2)
O6 0.0143(18) 0.022(2) 0.0204(19) 0.0042(15) 0.0076(15) -0.0014(15)
O6' 0.016(2) 0.030(3) 0.055(3) -0.009(2) -0.0025(19) 0.0047(18)
C1 0.032(4) 0.034(4) 0.022(3) -0.007(3) -0.002(3) 0.010(3)
C1' 0.040(4) 0.035(4) 0.022(3) -0.017(3) 0.014(3) -0.012(3)
C2 0.047(4) 0.033(4) 0.023(3) -0.014(3) 0.001(3) 0.010(3)
C2' 0.044(4) 0.022(4) 0.032(4) 0.002(3) 0.007(3) -0.011(3)
C3 0.028(4) 0.030(4) 0.050(5) -0.008(3) 0.020(3) -0.009(3)
C3' 0.018(3) 0.041(4) 0.047(4) -0.007(3) -0.002(3) 0.001(3)
C4 0.018(3) 0.014(3) 0.014(3) 0.000(2) 0.004(2) -0.002(2)
C4' 0.020(3) 0.013(3) 0.014(3) 0.000(2) 0.003(2) 0.000(2)
C5 0.016(3) 0.012(3) 0.025(3) 0.002(2) 0.002(2) 0.002(2)
C5' 0.015(3) 0.018(3) 0.018(3) 0.000(2) 0.007(2) -0.001(2)
C6 0.019(3) 0.018(3) 0.009(3) 0.003(2) 0.007(2) 0.002(2)
C6' 0.022(3) 0.020(3) 0.015(3) 0.001(2) -0.002(2) 0.000(2)
C7 0.022(3) 0.004(3) 0.016(3) -0.003(2) 0.005(2) 0.001(2)
C7' 0.014(3) 0.014(3) 0.022(3) -0.002(2) 0.001(2) 0.003(2)
C8 0.012(3) 0.015(3) 0.019(3) 0.000(2) 0.001(2) 0.001(2)
C8' 0.014(3) 0.016(3) 0.025(3) 0.007(2) 0.005(2) 0.001(2)
C9 0.012(3) 0.018(3) 0.007(2) -0.005(2) 0.0000(19) 0.001(2)
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C10' 0.018(3) 0.019(3) 0.011(3) 0.001(2) 0.000(2) -0.005(2)
C17 0.013(3) 0.021(3) 0.025(3) -0.006(2) 0.001(2) 0.001(2)
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C18 0.019(3) 0.036(4) 0.029(3) -0.003(3) 0.013(2) 0.001(3)
C18' 0.027(3) 0.030(4) 0.023(3) 0.007(3) -0.007(2) -0.008(3)
C19 0.024(3) 0.041(4) 0.018(3) -0.005(3) 0.008(2) 0.012(3)
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C21 0.018(3) 0.019(3) 0.015(3) -0.003(2) 0.001(2) 0.001(2)
C21' 0.026(3) 0.017(3) 0.021(3) -0.005(2) 0.004(2) -0.004(2)
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C24 0.028(4) 0.038(4) 0.041(4) -0.008(3) 0.004(3) 0.017(3)
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C26 0.028(3) 0.010(3) 0.015(3) 0.002(2) 0.002(2) -0.001(2)
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C27 0.026(3) 0.026(4) 0.027(3) -0.007(3) 0.004(3) -0.013(3)
C27' 0.030(3) 0.021(3) 0.017(3) 0.006(2) 0.005(2) 0.007(3)
C28 0.023(3) 0.015(3) 0.031(3) 0.001(2) -0.002(2) 0.003(2)
C28' 0.020(3) 0.029(3) 0.032(3) -0.012(3) 0.003(2) -0.001(3)
C46 0.034(4) 0.073(6) 0.039(4) 0.004(4) -0.016(3) -0.028(4)
C46' 0.070(6) 0.052(6) 0.095(7) -0.025(5) 0.055(6) -0.003(5)
C48 0.025(3) 0.030(4) 0.032(3) 0.000(3) 0.003(3) -0.011(3)
C48' 0.025(4) 0.033(5) 0.137(9) -0.017(6) 0.024(5) -0.007(4)
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 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix.  The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry.  An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.
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